hysics Lib.

MAY 3 1950

REGISTERED NO. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XXX] *SECTION A* [NO. 6

DECEMBER, 1949

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO,
SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES,
BANGALORE.

DIFFRACTION OF LIGHT BY TRANSPARENT SPHERES AND SPHEROIDS: THE FRESNEL PATTERNS

By Sir C. V. Raman and S. Ramaseshan

(From the Raman Research Institute and the Department of Physics, Indian Institute of Science, Bangalore)

Received December 7, 1949

1. Introduction

The phenomena with which we are concerned in the present paper are those arising when a beam of light emerges after traversing a sphere of radius large compared with the wave-length of light. Our attention was drawn to them in the course of some studies on the Christiansen experiment with spherules of glass described in a recent paper in these *Proceedings*. To elucidate more fully the effects described in that paper, it appeared to us desirable to examine the optical behaviour of an individual spherule of glass immersed in a liquid of nearly the same refractive index and traversed by light from a distant point source. Very pretty colour effects were observed with white light, which obviously had their origin in the fact that the convergence of the beam after its passage through the particle was widely different for the different rays of the spectrum. This suggested the use of a monochromatic light source, *e.g.*, a sodium vapour lamp. We then noticed that the light emerging from the spherule exhibits very characteristic diffraction patterns; the nature of these depends notably on the shape of the particle, being widely different for the two most interesting cases in which it is respectively a sphere and a spheroid of revolution. The configuration of the patterns changes progressively as the plane of observation is shifted away from the spherule; the difference in the refractive indices of the sphere and of the liquid in which it is immersed determines how rapid this change is. The diffraction patterns may be observed even when this difference is not small; their changes with the shift of the plane of observation are then rapid. The dispersive powers of the glass and the liquid not being the same, the difference in their refractive indices alters rapidly with the wave-length of the light employed. As a consequence, the patterns change quickly with the wave-length. This is readily observed when the light-source is a mercury arc, even without the aid of colour filters for selecting out the different spectral rays emitted by it.

Our observations were in the first instance made with the same tiny spherules of glass one millimetre in diameter as those used in the Christiansen experiment. We subsequently found, however, that essentially similar phenomena can be observed also with spheres which are still smaller, *viz.*, one-tenth of a millimetre in diameter and also with spheres of much larger size. A ball of quartz immersed in benzene shows the effects very well; its birefringence, however, results in two sets of patterns being observed instead of one, their separation varying with the direction in which the light traverses the sphere. It would seem that we have here a very simple and convenient method of observing and exhibiting the optical characters of a crystalline solid.

2. Geometric Theory

As we are concerned with spheres whose dimensions are great in comparison with the wave-length, it is justifiable, at least in the first instance, to regard the problem as one of geometrical optics, and then to supplement the results by considerations based on wave-theory. Using elementary methods, we may trace the course of a bundle of parallel rays incident on a transparent sphere and emerging therefrom. The deviation suffered is zero for the axially incident ray; it increases steadily and then much more rapidly as we approach the marginal ray which is incident tangentially on the surface. The deviations of the rays depend on the refractive index of the sphere relatively to that of the sorrounding medium. In the particular case when the relative index is unity, they vanish and the rays emerge again as a bundle of parallel rays. In the cases which interest us, the relative index is a little greater than unity, and the emerging beam would evidently be convergent, but such convergence would be very different for the axial bundle of rays and for the marginal ones. In actual practice, the sphere is immersed in a flat-walled cell completely filled with liquid. In tracing the course of the rays, the further deviations which occur when they emerge from the cell walls would also have to be considered.

The result of the passage of the light through the sphere and the enclosing liquid is most readily visualised by considering the cylindrical bundle of rays incident on the sphere to be divided up to a great number of concentric hollow cylindrical beams. Each such cylinder of rays would converge to a focus on the axis and subsequently diverge, but the focal points would all be different, being farthest from the sphere for the axial pencils and nearest to it for the marginal ones. In other words, instead of all the rays passing through the sphere converging to a single focus on the axis, we would have a continuous line of foci or concentration of intensity along the axial ray.

Further, since each hollow cylinder of rays emerges from the cell as a hollow cone of rays and the convergence of these is different, it follows that the successive cones would intersect each other and form a caustic surface, the cross-section of which by any plane normal to the axis would be a circle. The bundle of rays emerging from the sphere would therefore exhibit a concentration of intensity along its circular periphery. The area enclosed by this would be largest when the beam emerges from the cell and would contract as we recede therefrom, finally collapsing to a point when we reach the focus of the axially incident rays. Except in the limiting case when the relative index is unity, the diameter of the emergent beam would invariably be less than that of the sphere.

The foregoing remarks are illustrated by Fig. 1 below, in which the course of a bundle of parallel rays incident on a glass sphere of refractive index 1·54 immersed in water (refractive index 1·33) and emerging therefrom has been computed and shown. Besides drawing the course of the

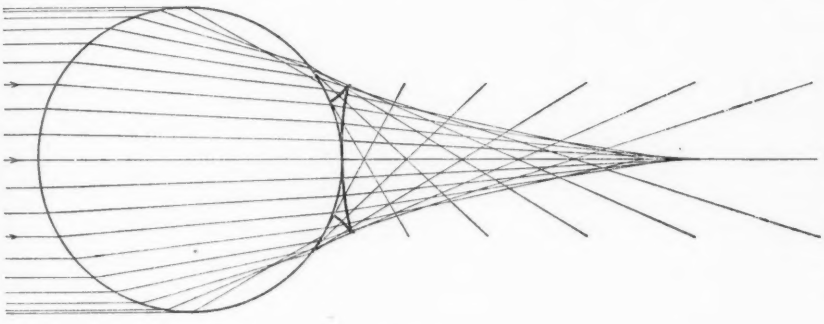


FIG. 1

rays, the form of the wave-surface immediately after emergence from the sphere has also been computed and drawn in. It exhibits the cusp-shaped form which in wave-theory corresponds to the formation of a caustic in geometrical optics.

3. INTERFERENCE PHENOMENA

As is evident from Fig. 1, the rays which have traversed the sphere by different paths intersect each other after emergence from it. It follows that interference effects should be observable. We may, in the first place, remark that wave-optical considerations reinforce the results indicated by the geometrical theory that there should be observable concentrations of intensity of *two* kinds in the light-field, firstly along the circular periphery

of the beam emerging from the sphere, and secondly along its axis. At the periphery of the beam, rays which have traversed closely adjacent and therefore nearly equal paths within the sphere intersect one other, while on the axis, rays meet which have transversed identically equal paths but emerge from different points forming a ring on the surface of the sphere. It follows that the axis should everywhere be a locus of maximum intensity, while the periphery should exhibit a maximum of intensity lying close to but not absolutely coincident with it. Corresponding to each of these two loci of maximum intensity, we should have a series of loci of subsidiary minima and maxima of intensity appearing at the points where the intersecting rays differ in optical path respectively by odd and even multiples of half a wave-length. In the case of the interferences running parallel to the circular periphery of the beam, it is evident that the intersecting rays meet at an angle which is small in its vicinity and increases as we move away from the periphery towards the centre of the field. It follows that the interference fringes running parallel to the circular caustic would be very wide at the margin at the field and becomes progressively narrower as we approach the centre of the light beam. The case is altogether different when we consider the interferences of the rays reaching points at and near the axis from points all round the circumference. These rays evidently meet at a fairly large angle which would change very little as we move away from the axis in any given plane of observation. It follows that the interference rings surrounding the axial concentration of intensity would be narrow, but evenly spaced. It is evident also that both the peripheral and axial sets of interference rings should widen out as we move away from the sphere and approach the focal point of the axial rays; for the angles of intersection of the interfering rays then steadily diminish. The superposition of the two sets of interference would obviously become most evident in the same circumstances.

It should not be supposed however, that elementary considerations of the kind indicated above would suffice completely to describe the actual facts of observation. In the first place, the approach is purely qualitative and makes no pretence of giving quantitative indications in respect of the intensity of illumination in the field. Indeed, even if it were to be developed so as to deal also with such questions, we should scarcely expect such a theory to be quite successful. The part of the area of the incident wavefront which gives rise to the experimentally significant phenomena is that which passes through the marginal regions of the sphere. This is a very small part of the whole, especially when the relative index of refraction is only a little greater than unity. Diffraction then necessarily plays a part

and determines the observed intensities of illumination in the field. We cannot therefore regard the geometrical approach to the problem as anything more than a useful and easily understood way of interpreting the observed phenomena.

4. Methods and Results of Observation

For observing the diffraction phenomena produced by a small spherule of glass, the most suitable procedure is to immerse it in a thin flat cell which is completely filled up with liquid and then covered by a glass-plate. The cell is then placed on the stage of a low-power microscope. A convenient light-source is provided by a small aperture backed by a sodium vapour lamp or alternatively a point-o-lite mercury arc. The former is most useful when it is desired to observe the patterns with light of one wave-length, while the latter (unless filters are used) is convenient for observing the patterns with several wave-lengths simultaneously. The light from the aperture is sent up through the cell by the plane reflecting mirror below the stage of the microscope, the condenser having been removed. By racking up the microscope, the patterns formed in the successive planes of observation commencing from the upper surface of the cell up to the focal point of the axial rays or even beyond may be conveniently observed. In the case of the larger spheres, no microscope is needed and the observations may be made with a suitable eyepiece or, better still, by receiving the light emerging from the sphere on a sheet of ground glass.

The experimental studies confirm the results of the foregoing theoretical discussion. The caustic and its accompanying interference fringes at the periphery of the field are readily observable features. The bright spot at the centre of the field indicated by the theory is first seen at some distance from the sphere and increases rapidly in intensity as we approach the focal point of the axial rays. That this spot is an optical image of the light source employed is readily verified by making the latter of triangular shape. The bright spot, if observed with a perfectly spherical particle, has then the same shape and increases progressively in size as we recede further and further from the sphere. It is important to remark that the bright spot continues to be visible along the axis of the beam even beyond the geometric focus of the axial rays. This clearly indicates that a purely geometric theory is insufficient to cover the facts.

To observe the uniformly spaced interference rings surrounding the bright central spot, one should use a very small aperture as the source. The necessity for this is easily understood, since the rings are closely spaced·

Both sets of rings can then be readily seen superposed on each other, especially as we approach the focal point of the axial rays.

Using an aperture backed by a mercury arc (without filters) as source, the caustics corresponding to the indigo, blue, green and yellow rays of the arc are seen well separated. With a quartz sphere, two sets of circular caustics are seen instead of one. That these represent the two refractive indices of the crystal corresponding to the direction of the incident beam is readily shown by placing a polaroid in the path of the incident light and rotating it. One or the other of the two caustics is then periodically extinguished.

It is very common to find particles having a spheroidal shape amongst those used for the Christiansen experiment. With such particles, the phenomena observed are strikingly different from those exhibited by spherical particles. The caustic appearing at the periphery of the emerging light beam is not circular but elliptic in shape, as is to be expected. Instead of the bright central spot given by a spherical particle, we find a light-figure having the shape of the geometric evolute of the boundary of the beam emerging from the spheroid. This is clearly a diffraction effect having its origin at the part of the wave-front which has traversed the interior of the particle near its margin, almost grazing the surface.

Summary

The paper describes and discusses the diffraction effects observed when a beam of light traverses a transparent sphere immersed in a liquid of slightly lower index and emerges therefrom. The two most interesting features are firstly, a concentration of intensity along the periphery of the emerging light beam which is evidently in the nature of a caustic and secondly, a concentration of intensity along the axial ray which is in the nature of a continuous focus. These two features are each accompanied by a set of interference-rings and these appear superposed on each other. Significant alterations appear in these features when the particle has a spheroidal shape. With a birefringent sphere, two sets of caustics are, in general, observed. 12 Photographs illustrate the paper.

Description of the Figures

Figs. 1, 2 and 3 in Plate V

Diffraction patterns with sodium light of a spherical glass ball one millimetre diameter immersed in xylene, the plane of observation being progressively removed further and further from the cell containing the sphere. Note the bright circular caustic with the accompanying fringes, and the central bright spot which progressively increases in intensity with increasing distance from the sphere.

FIG. 1

FIG. 4

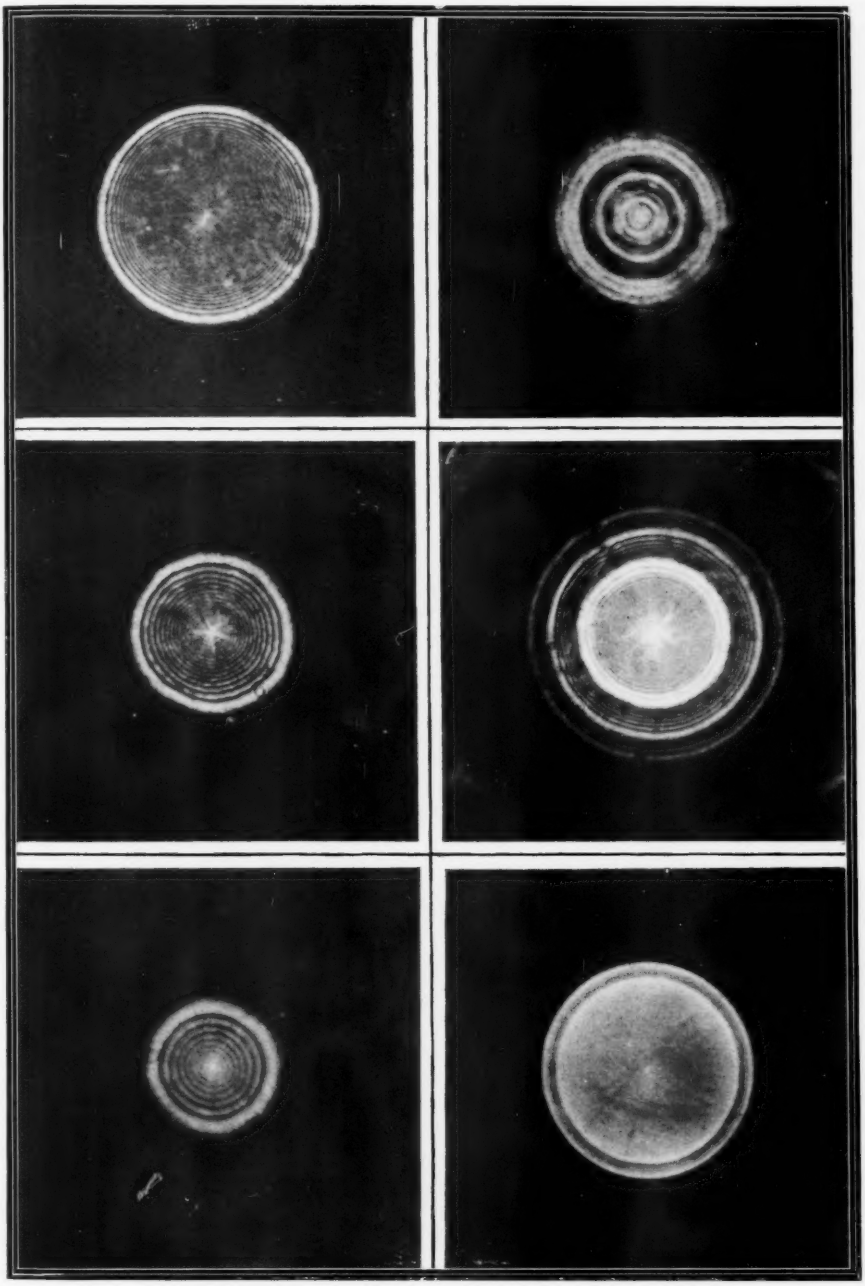


FIG. 2

FIG. 5

FIG. 3

FIG. 6

Diffraction by spheres immersed in a liquid.

FIG. 7

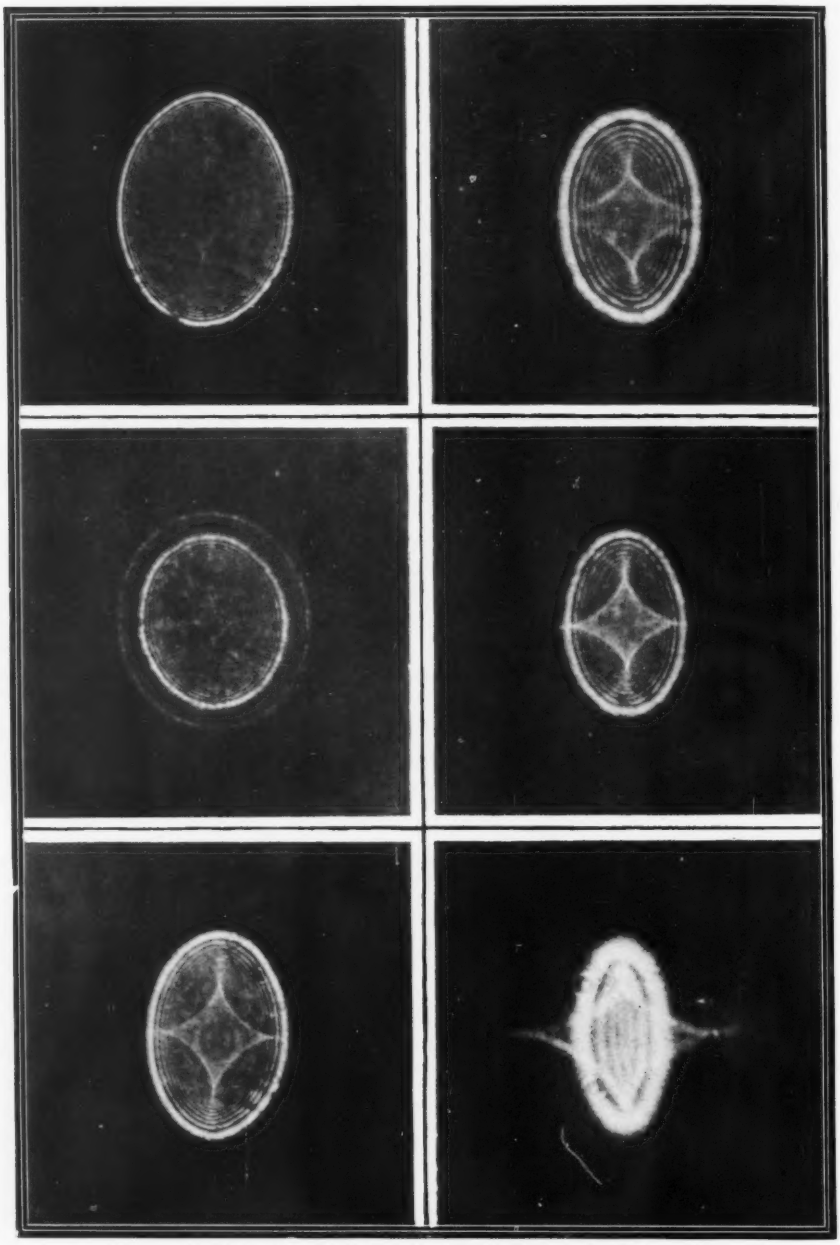
FIG. 10

FIG. 8

FIG. 11

FIG. 9

FIG. 12



Diffraction by spheroids immersed in a liquid

FIG. 4. Diffraction pattern with sodium light of a spherical ball immersed in nitrobenzene, the plane of observation being rather near the focal point of the axial rays. The pattern is highly magnified in the reproduction to exhibit the two superposed sets of interference-rings.

FIG. 5. Diffraction pattern of a sphere of glass one millimetre in diameter immersed in a nitrobenzene—monobromonaphthalene mixture, with an unfiltered mercury arc as source. The faint outer caustic is due to the λ 4046 radiation. The next bright caustic inside is due to the λ 4358 radiation, while those nearer the centre are due to the green and yellow radiations of the mercury arc.

FIG. 6. Diffraction pattern in sodium light of a quartz sphere of 5 centimetres diameter immersed in benzene. Notice the doubling of the caustic resulting from birefringence. The bright spot at the centre of the pattern is clearly seen.

FIGS. 7, 8, 9, 10, 11 and 12 in Plate VI

Diffraction patterns of a spheroidal ball. All were obtained with sodium light except Fig. 8 which was recorded with a mercury arc and exhibits the caustics due to λ 4046 and λ 4758 separately. The immersion liquid was xylene in all cases except Fig. 12 which was obtained with a nitrobenzene—monobromonaphthalene mixture and has been reproduced on a highly magnified scale.

THERMAL EXPANSION OF FLUORSPAR AND IRON PYRITE

By D. C. Press

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received October 26, 1949

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

As early as 1908, Grüneisen showed that for a number of pure metals the ratio of the coefficient of thermal expansion to the specific heat was practically constant. Later, he (Grüneisen, 1912) gave a theory of the solid state and deduced a relation between the thermal expansion of a solid and its other physical properties. This law in its simplest form can be stated thus; $\gamma = \frac{V_0 \alpha}{\chi_0 C_v}$, where α, χ_0, C_v are respectively the coefficient of cubical expansion, the compressibility and the specific heat at constant volume of the solid. γ is a constant for any given substance. The value of γ for many substances lies between 1·5 and 2·5. It can be evaluated from the preceding relation if α, χ_0 and C_v are known. The present investigation on thermal expansion of the crystals of fluorspar (CaF_2) and iron pyrite (FeS_2) was undertaken with a view to ascertain the applicability of the Grüneisen law to these crystals.

2. Previous Work

Flourspar.—Thermal expansion of fluorspar has been measured by a few workers. Fizeau (1868) using the method of interference of light, obtained $19 \cdot 11 \times 10^{-6}$ for the coefficient of linear expansion at a temperature of 40° C. Weidman (1889) obtained a value of $19 \cdot 34 \times 10^{-6}$ at a temperature of 52° C. The recent measurements are those of Valentiner and Wallot (1915). They have measured the expansion of fluorspar using Fizeau's interference method in the range from − 190° C. to 17° C., the value of α_l ranging from $7 \cdot 17 \times 10^{-6}$ to $18 \cdot 53 \times 10^{-6}$.

Pyrite.—Fizeau has also measured the thermal expansion of iron pyrite. He obtained a value of $9 \cdot 07 \times 10^{-6}$ at 40° C. Valentiner and Wallot (1915) have measured the expansion of this crystal also in the range − 175° C. to 18° C. and their values of α_l increase steadily from $2 \cdot 95 \times 10^{-6}$ to $8 \cdot 43 \times 10^{-6}$ in this range.

No data on the thermal expansion of these crystals at high temperatures are available in the literature. It was, therefore, found desirable to extend these measurements in the range of higher temperatures. The present work deals with the method and description of the technique used in measuring the thermal expansion of fluorspar and iron pyrite in the range 30° C. to 300° C.

3. Details of the Experiment

In the present investigation, the well-known interferometric method was used. Instead of measuring the differential expansion between the solid and some other standard substance, the absolute expansion of the solid was directly measured. As this method has been fully described in the literature (Merritt, 1933) it has been considered unnecessary to repeat the same here.

The furnace with the interferometer plates in position is illustrated in Fig. 1. The optical arrangement employed in the present investigation is shown in Figs. 2 and 3. As there was no elaborate set-up, as described in Tutton's book on Crystallography, at the disposal of the author, the entire apparatus was assembled from component pieces available in the laboratory. In view of this, all the necessary precautions were taken to see that the measurements were not vitiated by errors of any kind.

Preparation of the specimens.—Both fluorspar and iron pyrite possess cubic structure. The pyrite crystals were rectangular in shape, the edges measuring 0·7 to 1·0 cm. Three good samples were selected and one face of each was ground and polished flat. By grinding the sides, each one of them was formed into a small cylinder with a flat base and a small cone terminating in a point at the top. The base was about 6 mm. in diameter and the height about 5 mm. A micrometer screw gauge reading to 1/4000 cm. was used to measure the height of the samples. The heights were adjusted equal to each other as far as the micrometer screw could tell. Further finer adjustments in their heights were made by viewing the interference fringes. In the case of flourspar, a nearly flat parallel sided clear crystal was used. It was a little over 2·5 cm. in length and about 1·0 cm. thick. It was cut into three pieces at right angles to the flat sides and three specimens equal in height were prepared as in the case of pyrite. The specimens were necessarily made very small so that they may acquire the temperature of the furnace as quickly as possible.

Probable errors and their elimination.—Although the principle of the interferometric method of measuring thermal expansion is a simple one,

there are various stages in the experimental procedure where errors creep in. These are discussed in some detail below:—

When the temperature was raised it was noticed at times that there was a gradual change in the width and orientation of the fringes. In order

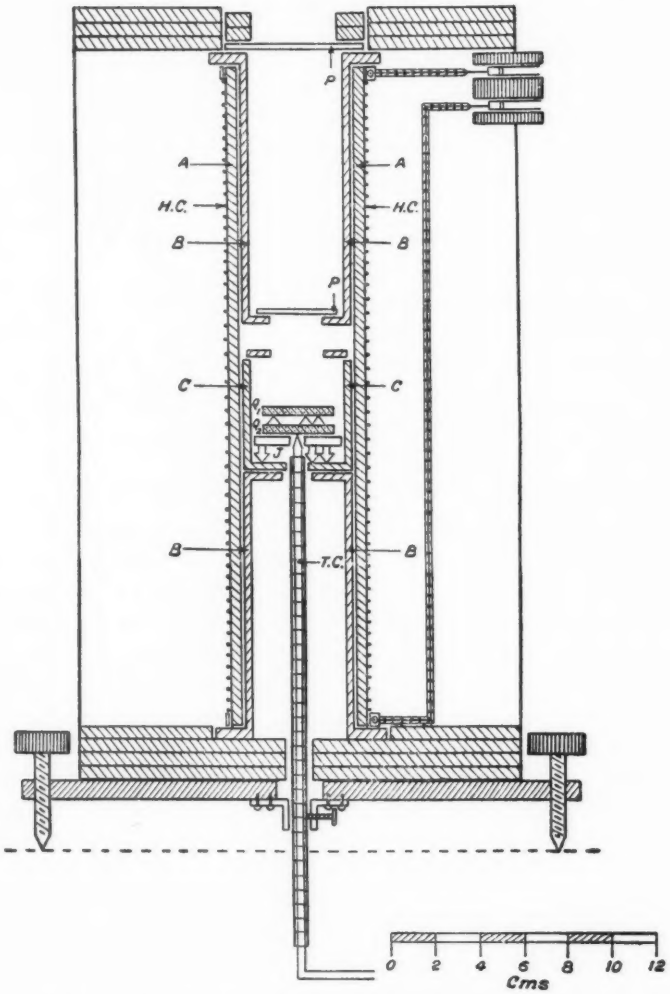


FIG. 1. *The Furnace.*— *A-A*—Porcelain tube, *B-B*—Porcelain support, *C*—Porcelain cup, *H.C.*—Heater coil, Q_1, Q_2—Interferometer plates, *J*—tripod base, *T.C.*—Thermo-couple, *P*—Glass discs.

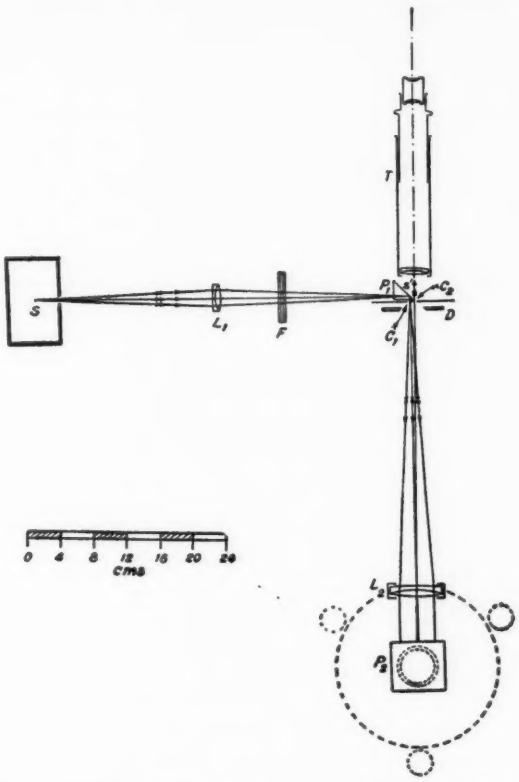


FIG. 2. *Optical Arrangement.*—*S*—A small aperture behind which a mercury arc was kept. L_1, L_2—Lenses, P_1, P_2—Right-angled prisms. *D*—diaphragm, C_1, C_2—Apertures. F = Zeiss mercury green filter. T = telescope.

to eliminate these errors arising from changes in the thickness of the surface films at the points of contact between the discs and the specimens and tilting of the individual specimens, the following precautions were taken:—

(1) The area of the points of contact between the specimens and the upper interferometer disc was made very small.

(2) A preliminary heat treatment was given to the interferometer by heating it to the highest temperature up to which measurements would be taken subsequently and by allowing it to cool down.

(3) One of the specimens was made very stable by placing an additional load over it and to make observations at the point of contact between this specimen and the upper disc.

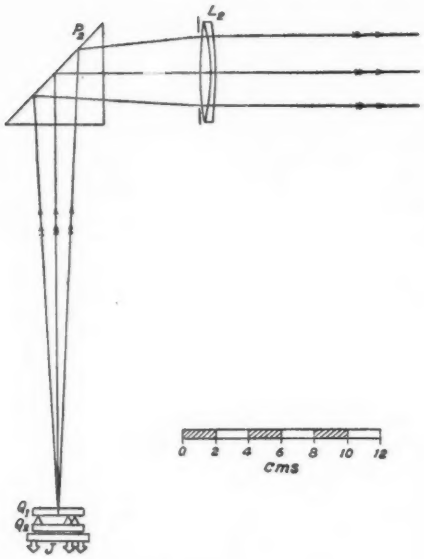


FIG. 3.

The errors, if any, in the measurements of the temperature of the specimen were reduced to a minimum (1) by making the specimens sufficiently small without impairing their mechanical stability, (2) by winding the furnace with a few more turns of the heating wire near the ends, so as to get a uniform temperature throughout the middle portion of the furnace and (3) by using a low rate of heating.

When the temperature of interferometer system is raised, the refractive index of air changes which in its turn gives rise to a change in the wave-length of light. Therefore a correction would have to be applied. A simple calculation shows that to a first approximation

$$\frac{\Delta L}{L} = \frac{\bar{\lambda}}{2L} \cdot \Delta N + (n_0 - 1)\frac{273P}{760}\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \qquad (1)$$

where L is the separation between the two interferometer discs at temperature T_1 and $L + \Delta L$ at T_2, P = the pressure of the atmosphere, ΔN = the number of fringes which pass the fiducial mark, $\bar{\lambda}$ = the wave-length of the radiation in vacuum, n_0 = the refractive index of air at 273° K. and 760 mm. of mercury. The second term on the right-hand side of equation (1) represents the correction to be applied for the change of wave-length in air on account of the change in its temperature.

Meggers and Peters (1918) have measured the refractive index of air for different wave-lengths at 0°, 15° and 30° C. and under a pressure of 760 mm. mercury. From the formulæ and the table given in their paper one can calculate the values of $\bar{\lambda}$ and n_0 corresponding to the wave-length 5460·7 Å of the green mercury line. Thus

$$\bar{\lambda} = 5462{\cdot}2 \text{ Å} \quad \text{and} \quad n_0 - 1 = 2924{\cdot}9 \times 10^{-7}.$$

4. Results

The necessary readings to be taken during the run of the experiment are:—

(1) The number of the interference fringe occupying a fixed position with reference to the fiducial mark.

(2) The reading of the microammeter just at the moment when an interference fringe occupies the desired position.

(3) The temperature of the cold-junction of the thermocouple.

The microammeter readings were taken when successive fringes occupied a definite position with respect to the fiducial mark. These data were then plotted and the temperatures corresponding to the fringes at regular intervals were obtained from the graphs and are listed in Tables I and III. The third column gives the value of the increment and the fourth one gives the total increase in length per unit length. By plotting the values given in the last column against temperature, the values of $\frac{\Delta L}{L_0}$ at various temperatures were

Table I

Relative change of length for fluorspar

$L_0 = 0{\cdot}5497$ cm. $\qquad \frac{\bar{\lambda}}{2L_0} = 0{\cdot}00004969$

Number of the fringe ΔN	Temperature °C.	Air correction	$\frac{\bar{\lambda}}{2L_0} \cdot \Delta N$	$\frac{\Delta L}{L_0}$
0	30·4	0	0	0
10	55·0	0·000018	0·000497	0·000515
20	79·4	0·000033	0·000994	0·001027
30	103·1	0·000046	0·001491	0·001537
40	126·3	0·000057	0·001988	0·002045
50	149·8	0·000067	0·002485	0·002551
60	172·8	0·000076	0·002981	0·003057
70	195·7	0·000084	0·003478	0·003562
80	217·7	0·000091	0·003975	0·004066
90	240·1	0·000097	0·004472	0·004569
100	262·3	0·000103	0·004969	0·005072

TABLE II

Coefficient of thermal expansion of flourspar

Temperature °C.	$\frac{\Delta L}{L_0}$ As obtained from graph	$\alpha_l \times 10^6$ At mean temperature	Temperature °C.	$\frac{\Delta L}{L_0}$ As obtained from graph	$\alpha_l \times 10^6$ At mean temperature
40	$19{\cdot}95 \times 10^{-5}$		210	388·1	22·85
50	40·6	21·40	230	433·8	
70	83·4		250	480·0	23·80
90	125·7	21·40	270	527·6	
110	168·5				
130	211·5	21·65			
150	254·8				
170	298·7	22·25			
190	343·2				

TABLE III

Relative change of length for iron pyrite

$L_0 = 0{\cdot}5077$ cm. $\qquad \frac{\bar{\lambda}}{2L_0} = 0{\cdot}00005380$

Number of the fringe ΔN	Temperature °C.	Air correction	$\frac{\bar{\lambda}}{2L_0} \cdot \Delta N$	$\frac{\Delta L}{L_0}$
0	27·8	0	0	0
8	74·2	0·000032	0·000430	0·000462
16	119·2	0·000056	0·000861	0·000917
24	161·3	0·000074	0·001291	0·001365
32	203·4	0·000088	0·001722	0·001810
40	243·2	0·000100	0·002152	0·002252
48	281·5	0·000109	0·002583	0·002692
50	291·1	0·000112	0·002690	0·002802

TABLE IV

Coefficient of thermal expansion of iron pyrite

Temperature °C.	$\frac{\Delta L}{L_0}$ As obtained from graph	$\alpha_l \times 10^6$ At mean temp.	Temperature °C.	$\frac{\Delta L}{L_0}$ As obtained from graph	$\alpha_l \times 10^6$ At mean temp.
30	$2{\cdot}70 \times 10^{-5}$		170	145·20	10·70
50	22·20	9·85	190	166·60	
70	41·90		210	188·20	11·00
90	62·00	10·13	230	210·20	
110	82·25		250	233·00	11·50
130	103·00	10·50	270	256·00	
150	124·00				

read off from the resulting graphs. The linear coefficient of thermal expansion was calculated for various temperatures and the values are given in Tables II and IV. Figs. 4 and 5 show graphically the relation between α_l and temperature for fluorspar and iron pyrite respectively.

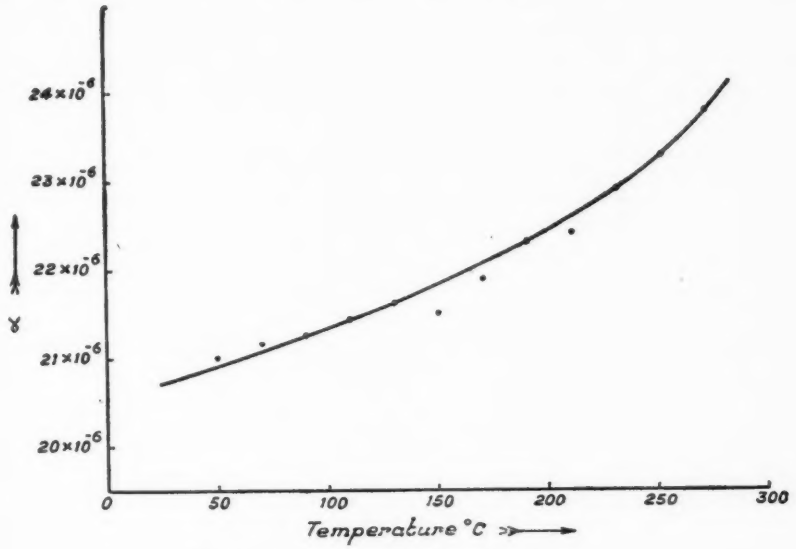


FIG. 4. Thermal Expansion of Fluorspar

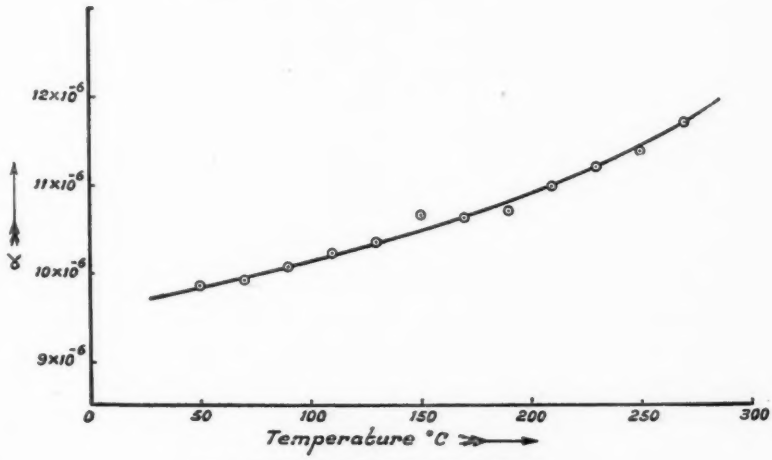


FIG. 5. Thermal Expansion of Iron Pyrite

5. Discussion

As pointed out in the introduction, according to Grüneisen, γ should be a constant for a given solid independent of temperature. We shall now proceed to see whether this law holds good for fluorspar and iron pyrite. Taking $\gamma = 1{\cdot}7$, Grüneisen satisfactorily explained the existing data on the thermal expansion of fluorspar and iron pyrite due to Valentiner and Wallot (1915) in the reigion from $-180°$ C. to 0° C. A satisfactory test of the relation should require data above the room temperature also. This has been done in the present investigation.

The Grüneisen constant has been evaluated in the temperature region 20° C. to 300° C. and the values are given in Tables V and VI. For V_0, the molecular volume, the values used are 24·5 c.c. for CaF_2 and 24·1 c.c. for FeS_2. Strictly speaking, V_0 is the molecular volume at the absolute zero of temperature and under zero external pressure, whereas the values used are those at room temperature and atmospheric pressure. For χ_0, the compressibility, the values obtained by Bridgman (1925) at room temperature and atmospheric pressure have been used. According to Bridgman, $\chi = 1{\cdot}23 \times 10^{-12}$ cm.^{2} dyne^{-1} for CaF_2 and $\chi = 0{\cdot}71 \times 10^{-12}$ cm.^{2} dyne^{-1} for FeS_2 at 30° C. The values of C_v have been calculated from the measured values of C_p using the relation $C_p - C_v = AC_p^2 T$. For CaF_2 the values of C_p as obtained by Naylor (1945) have been used. Thus

$$C_p = 14{\cdot}30 + 0{\cdot}00728T + \frac{46900}{T^2} \text{ cals. per mol. per deg.}$$

$$(298° \text{ K} \leqslant T \leqslant 1424° \text{ K})$$

$$\text{and } C_p - C_v = 5{\cdot}36 \times 10^{-6} C_p^2 T.$$

For FeS_2 the values of C_p obtained by Kelley (1934) have been used. Thus

$$C_p = 10{\cdot}70 + 0{\cdot}01336 \text{ T cals. per mol. per degree}$$

$$(270° \text{ K} \leqslant T \leqslant 773° \text{ K})$$

$$\text{and } C_p - C_v = 2{\cdot}72 \times 10^{-6}. C_p^2 T$$

The values of γ in the region below the room temperature have also been calculated and given in Tables V and VI. For this purpose the values of α_l obtained by Valentiner and Wallot (1915) have been used, while for C_v the values are taken from Landolt and Bornstein Tables (1931) which are based on the experimental results of Eucken and Schwers (1913).

The results clearly show that γ is not a constant but varies with temperature. In the case of CaF_2, it increases steadily from 1·81 to 1·96 in the

TABLE V

Fluorspar

$V_0 = 24{\cdot}5$ c.c $\qquad \chi_0 = 1{\cdot}23 \times 10^{-12}$ cm.^{2} dyne^{-1}

Temp. °C.	C_p	C_v	α_l	$\gamma = \frac{3\alpha_l V_0}{\chi_0 C_v}$
−178·6	6·45	6·43	$7{\cdot}17 \times 10^{-6}$	1·60
−115·7	10·94	10·84	13·02	1·72
− 63·2	13·69	13·48	16·04	1·71
− 17·4	15·45	15·12	17·58	1·67
+ 20	16·979	16·527	20·81	1·81
60	17·147	16·623	21·40	1·84
100	17·352	16·751	21·40	1·84
140	17·582	16·898	21·65	1·85
180	17·827	17·056	22·25	1·87
220	18·081	17·218	22·85	1·90
260	18·345	17·384	23·80	1·96

TABLE VI

Iron pyrite

$V_0 = 24{\cdot}1$ c.c. $\qquad \chi_0 = 0{\cdot}71 \times 10^{-12}$ cm.^{2} dyne^{-1}

Temp °C.	C_p	C_v	α_l	γ
−165·0	5·25	5·24	$2{\cdot}95 \times 10^{-6}$	1·3
−118·0	9·02	8·99	5·16	1·40
− 35·6	13·08	12·97	7·73	1·45
+ 20	14·615	14·444	9·65	1·63
60	15·149	14·941	9·85	1·61
100	15·683	15·434	10·13	1·60
140	16·218	15·922	10·50	1·60
180	16·752	16·406	10·70	1·59
220	17·287	16·886	11·00	1·60
260	17·821	17·361	11·50	1·62
300	18·355	17·830	12·20	1·66

range 20° C. to 260° C. In the case of FeS_2 there is first a slow decrease in the range 20° C. to 100° C., then remaining constant in the range 100° C. to 200° C., while above this range there is a rapid increase. The Grüneisen's assumption that γ is a constant for a given solid is not at all valid.

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman who suggested the problem and to Prof. R. S. Krishnan for valuable discussions.

SUMMARY

The paper describes the measurements of the thermal expansion of crystals of fluorspar and iron pyrite over the range of temperature from

40° C. to 300° C. by a modification of Fizeau's interference method. In the case of fluorspar, the linear coefficient of expansion has been found to increase steadily from $20{\cdot}9 \times 10^{-6}$ to $23{\cdot}8 \times 10^{-6}$ in the range from 40° C. to 260° C. while in the case of pyrite the linear coefficient increases from $9{\cdot}7 \times 10^{-6}$ to $11{\cdot}5 \times 10^{-6}$ in the same range. Using the measured values of the coefficients of thermal expansion and the known values of C_v, the Grüneisen constant γ has been evaluated for both the crystals. It is found that γ is not a constant but varies markedly with temperature.

References

1. Bridgman .. *Amer. Journ. Sci.*, 1925, **10**, 483.
2. Eucken and Schwers .. *Verh. der Deuts. Ges.*, 1913, **15**, 583.
3. Fizeau .. *Ann. der Physik.*, 1868, **135**, 372.
4. Grüneisen .. *Ibid.*, 1912, **39**, 257.
5. Kelley .. *U. S. Bureau Mines Bull.*, 1934, No. 371.
6. Landolt Bornstein .. *Phys. Chem. Tabellen*, II Erganz, 1931, 1244.
7. Meggers and Peters .. *Sci. Pap. Bur. Stds.*, 1918–19, **14**, 697.
8. Merritt .. *Journ. Bur. Stds.*, 1933, **10**, 59.
9. Naylor .. *Journ. Amer. Chem. Soc.*, 1945, **67**, 150.
10. Valentiner and Wallot .. *Ann. der Physik*, 1915, **46**, 837.
11. Weidman .. *Ibid.*, 1889, **38**, 453.

SAPPHIRINE—(*Madura*)

By Prof. T. N. Muthuswami, M.A., F.A.Sc.
(Department of Geology, Presidency College, Madras)

Received July 29, 1949

Occurrence

Sapphirine, a silicate of aluminium and magnesium $Mg_5Al_{12}Si_2O_{27}$, has been found in a thin band of hypersthene granulite in an abandoned quarry about a mile north of the village of Ganguvarpatti, Madura District.

The quarry was opened a decade ago as the rock found commercial value as a touchstone, and has since been abandoned as the band was too limited in extent for development.

The only other reported occurrence in India is by Walker and Collins from Vizagapatam District.

Country Rock

The country rock in which this band occurs is made up of medium to coarse-grained garnetiferous biotite schists and cordierite biotite gneisses. The mineral constituents include biotite, phlogopite, garnet, hypersthene, anthophyllite, cordierite, sillimanite, spinel and sapphirine. The mineral assemblage places the rock in the zone of high-grade metamorphism.

Mineralogy of Sapphirine

The following is a general description of the mineral:

Physical Properties

Dark blue, generally subhedral; rarely in euhedral prismatic forms; sub-vitreous lustre; dull and greasy on freshly broken irregular surfaces; no cleavage observed; $H = 7{\cdot}5 - 8$; $G = 3{\cdot}58$.

Optical Properties

The greatest and least indices of refraction were determined at room temperature (32° C.) by liquids; n_β was determined from the nomogram of optic axial angle formula; the birefringence was checked in section by Berek Compensator; the optic axial angle was determined by the use of Universal stage.

Table I gives the properties of sapphirine from Madura, Vizag and two foreign localities.

TABLE I

Optical Properties of Sapphirine

	Madura	Vizagapatam	Dangin	Transvaal
n_α ..	1·717	1·714	..	1·714
n_β ..	1·722	1·718	1·720±0·002	1·719
n_γ ..	1·724	1·720	..	1·720
Birefringence ..	0·007	..	..	..
Sign ..	Negative	Negative	Negative	Negative
2V ..	64°	62°	50°	50·5°
X ..	Colourless	Pinkish grey	Colourless	Pale pinkish buff
Y ..	Lavendar blue	Cobalt blue	Blue	Pale cerulean blue
Z ..	Azure blue	Prussian blue	Deep blue	Italian blue
ZVC' ..	..	15°	7°	6°

Intergrowth and Related Structures

The mineral is seen to occur in the slides:—

(1) as a diffuse growth from various centres,

(2) as a wart-like symplektite with hypersthene,

(3) as needles and laths projecting into the cleavages of hypersthene, giving a ribbed texture,

(4) as fan-shaped symplektites with hypersthene showing dactylitic texture,

(5) as myrmekitic intergrowths with cordierite,

(6) as replacing spindles of spinel.

The needles and laths of sapphirine are seen penetrating into biotite from hypersthene. The needles in both the minerals are in optical continuity. The mineral never penetrates into garnet. The pink colour of hypersthene is masked by the blue sapphirine where the intergrowth is intimate.

CHEMICAL DATA

The chemical analysis of the mineral under study (column 10) is given in Table II with other available data.

TABLE II

Chemical Analysis

(Sapphirine)

	1	2	3	4	5	6	7	8	9	10
SiO_2 ..	12·83	12·95	12·95	13·44	14·56	14·51	14·76	14·86	14·89	16·00
P_2O_5 ..	..	..	.	..	..	..	..	..	0·10	..
Al_2O_3 ..	65·29	64·44	62·38	62·98	60·49	63·11	63·23	63·25	60·44	55·56
Fe_2O_3 ..	0·93	..	1·69	..	..	.	..	..	1·70	2·72
FeO ..	0·65	1·66	3·09	9·08	7·65	3·92	1·65	1·99	6·45	8·35
MgO ..	19·78	19·83	15·22	15·28	17·13	16·85	19·75	19·28	15·23	17·16
CaO ..	..	..	..	..	..	0·38	..	..	..	..
Na_2O ..	..	..	trace	..	..	..	..	..	0·21	..
K_2O ..	..	..	0·10	..	..	..	..	..	0·02	..
TiO_2 ..	..	..	..	..	..	..	..	..	0·04	0·22
MnO ..	..	..	trace	..	..	0·53 Mn_2O_3	..	..	0·20	0·02
H_2O+ } ..	*0·31	*0·34	4·80	..	*0·56	*0·49	..	..	0·57	0·14
H_2O- }			0·05	..					0·41	nil
Total ..	99·79	99·22	100·28	100·78	100·39	99·79	99·39	99·38	100·26	100·17
Author ..	Ussing	Lorenzen	E.D. Mountain	Warren	Walker & Collins	Stromeyer	Schluttig	Damour	R.T. Prider	T.N.M. Swami
Sp. Gr. ..	3·486	3·460	3·398	3·50	3·542	..	..	3·473	3·554	3·58

* = Loss on ignition

1. Mineral from Fiskernas, Greenland, Ussing, *Zs. Kr.*, **15**, 600.
2. ,, ,, ,, Lorenzen, *Medd. Gronl.*, **7**, 184.
3. ,, Blinkwater, Transvaal, Edgar, D. Mountain, *Miner. Mag.*, 1939, **25**, 280.
4. ,, St. Urbain, Quebec, Charles H. Warren, *Am. Jour. Sc.*, 1912, **33**, 4th Ser. 272.
5. ,, Vizagapatam, S. India, Walker, T. L., and Collins, W. H., *Rec. Geol. Surv. of India*, 1907, **36**, Part p. l.
6. ,, Fiskernas, Greenland, Stromeyer, Unters, *Misch. Mineralk*, 1871, **391**.
7. ,, ,, ,, Schluttig, *Inaug. Diss., Leipzig*, 1884, **22** and *Zs. Kr.*, **13**, 74.
8. ,, ,, ,, Damour, *Bull. Soc. Geol.*, vi., 1849, 315.
9. ,, Dangin, W. Australia, Prider, R. T., *Geol. Mag.*, 1945, 49/54, **82**.
10. ,, Ganguvarpatti, S. India, (Madura) This paper.

The structural formula is calculated after deducting Fe_2O_3 and H_2O which are considered as limonitic impurities.

TABLE III

Structural Formula

Sapphirine : Madura

	Weight per cent.		Molecular proportion	Metal atoms on basis of 10 (O)		Metal groups
	I	II				
SiO_2 ..	16·00	16·44	0·2740	0·981		1·00
TiO_2 ..	0·22	0·22	0·0027	0·010		
Al_2O_3 ..	55·56	57·11	0·5599	4·009	0·009 / 4·000	4·00
Fe_2O_3 ..	2·72	..	..	..		
FeO ..	8·35	8·58	0·1191	0·426		2·00
MgO ..	17·16	17·64	0·4410	1·579		
MnO .	0·02	0·02	..	..		
CaO ..	..	..	..	..		
H_2O+ ..	0·14	..	..	..		
H_2O- ..	..	..	..	..		
Total ..	100·17	100·01	$(Mg.Fe'')_2$	$(MgFe'')_3$	$Al_4 \cdot Si \cdot Ti \cdot Al \cdot O_{10}$	

I. Sapphirine from sapphirine-biotite rock, Madura, *Analyst*, J. H. Scoon, Cambridge.

II. Analysis I, recalculated to 100 after removal of Fe_2O_3 and water.

ASSOCIATED MINERALS

Sapphirine is associated with the following minerals:—

Hypersthene, anthophyllite, cordierite, biotite, garnet and spinel.

TABLE IV

Optical Properties of Hypersthene, Anthophyllite and Cordierite

(Associated with Sapphirine—Madura)

	Hypersthene	Anthophyllite	Cordierite
X ..	Pink	Pale yellow	Yellowish white
Y ..	Yellow	Light brown	Violet
Z ..	Green	Brown	Violetish blue
2V ..	88°	82°–84°	70°–81°
Birefringence ..	0·0107	0·024	0·0086
Sign ..	Negative	Positive	Positive
Other characteristics	Rectangular microplakite inclusions	: :	Numerous pleochroic haloes, around zircon monazite and apatite
	Relics of anthophyllite	: :	Polysynthetic twinning lamellæ
	Cleavages of anthophyllite–126° and 54°	Hypersthene-anthophyllite symplektite observed	Pinitization along cracks
	In intergrowth with sapphirine and spinel		As myrmekite with sapphirine
			Encloses blebs of hypersthene

Table IV shows the optical characters of the first three minerals. The Universal stage and the Berek Compensator were used for the determination of 2V and birefringence respectively.

Biotite

The mineral is found as laths intruded by idiomorphic prisms of sapphirine; and at contacts between garnet and cordierite as a reaction product. It is strongly pleochroic in tones of yellow to brown.

Garnet

Occurs in big sizes, with cracks and ruby-red colour; is markedly idioblastic against intergrowths of hypersthene and spinel.

Spinel

Is green and rather opaque in somewhat thick sections, with grains of iron ores in cracks; occurs in granules as intergrowth with hypersthene and in part replaced by sapphirine.

Magnetite and apatite occur as minor accessories.

Origin of Sapphirine

Walker has ascribed a contact metamorphic origin to the sapphirine from Vizagapatam. The ultra-basic spinel bearing rocks of the charnockite series are considered to have reacted with sillimanite schists to give rise to sapphirine. Steenstrup also attributed a metamorphic origin to the sapphirine from Fiskernas in Greenland. He postulates high MgO, high Al_2O_3 and low SiO_2 in the original rocks. Warren describing the origin of sapphirine with ilmenite rocks near St. Urbain, Quebec, considers the mineral to be of magmatic origin. He does not however rule out the possibility of its being a reaction product between spinel and feldspar.

In this area, the origin of sapphirine has to be studied in the light of the associated minerals:—

Cordierite occurs with sillimanite in some rocks, and in such cases the other associated minerals are hypersthene, garnet, biotite, orthoclase and quartz.

The cordierite owes its origin to the metamorphism of pelitic sediments with chloritic mixtures.

$$\begin{aligned} &6 \times 2H_2O\ Al_2O_3\ 2SiO_2 + 2 \times 2H_2O\ 3\ MgO\ 2\ SiO_2 \\ &\quad 6 \text{ kaolin} \quad + \quad 2 \text{ chlorite} \\ &= 3 \times 2\ MgO\ 2\ Al_2O_3\ 5\ SiO_2 + SiO_2 + 16\ H_2O \\ &\quad 3 \text{ cordierite} \quad + \quad \text{quartz} + 16 \text{ water} \end{aligned} \qquad (1)$$

K, Al and Si constituents accounted for below will give rise to biotite, sillimanite and quartz.

$$1 \times K_2O\ Al_2O_3\ 6\ SiO_2 + 3 \times 2\ MgO\ 2\ Al_2O_3\ 5\ SiO_2 + 2\ H_2O$$
orthoclase + 3 cordierite + 2 water

$$= 2\ H_2O\ K_2O\ 6\ (Mg, Fe)O\ Al_2O_3\ 6\ SiO_2 + 6 \times Al_2O_3\ SiO_2 + 9 \times SiO_2$$
biotite + 6 sillimanite + 9 quartz (2)

The spinel bearing types with hypersthene would indicate magnesia metasomatism. The magnesia influx has obviously been derived from the pink granitized zone of the area.

$$1 \times 2\ MgO\ 2\ Al_2O_3\ 5\ SiO_2 + 5\ MgO = 5 \times MgO\ SiO_2 + 2 \times MgO\ Al_2O_3$$
cordierite + 5 magnesia = 5 hypersthene + 2 spinel (3)

The basic front of the granitization referred to has given rise to the hypersthene spinellite situated far away from the loci of granitization.

Sapphirine occurs in rocks intimately associated with hypersthene spinellite. It is always accompanied by biotite. K, Al and Si constituents in the vanguard of the basic front have given rise to sapphirine, biotite and cordierite. Thus,

$$25 \times (Mg\ Fe)O\ SiO_2 + 36 \times MgO\ Al_2O_3 + 5 \times K_2O\ Al_2O_3 6\ SiO_2 + 10\ H_2O$$
25 hypersthene + 36 spinel + 5 orthoclase + 10 water
(Hypersthene spinellite)

$$= 5 \times 2\ H_2O\ K_2O\ 6\ (Mg, Fe)O\ Al_2O_3\ 6\ SiO_2 + 5 \times 5\ MgO\ 6\ Al_2O_3\ 2\ SiO_2 + 3 \times 2\ MgO\ 2\ Al_2O_3\ 5\ SiO_2$$
5 biotite + 5 sapphirine + 3 cordierite (4)

The extent of the above transformation depends not only on the availability of the metasomatising fluids but also on the weak spots of the minerals such as defective lattices, cleavages and cracks.

Sapphirine shows a rapid growth as finger-like processes along the cleavages of hypersthene giving rise to the ribbed texture. It shoots itself into biotite. The defective crystal lattices have been taken by sapphirine giving rise to blurred contacts and intergrowth textures with cordierite, spinel and hypersthene.

Thus sapphirine in this case is believed to be due to metasomatic metamorphism.

ACKNOWLEDGMENT

The writer is grateful to Professor C. E. Tilley, F.R.S., for helpful criticism on the mineral assemblage after going through the micro-sections.

FIG. 1. x 35

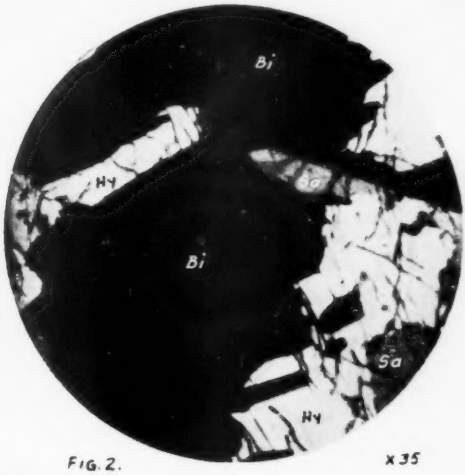


FIG. 2. x 35

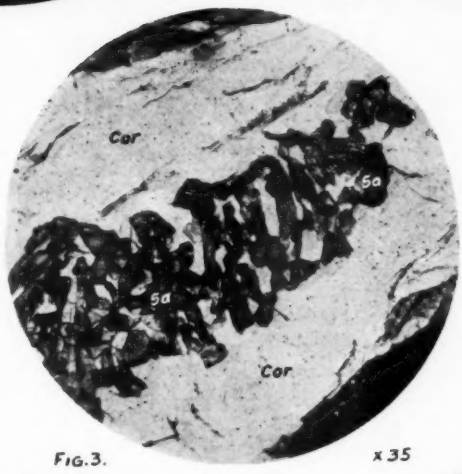


FIG. 3. x 35

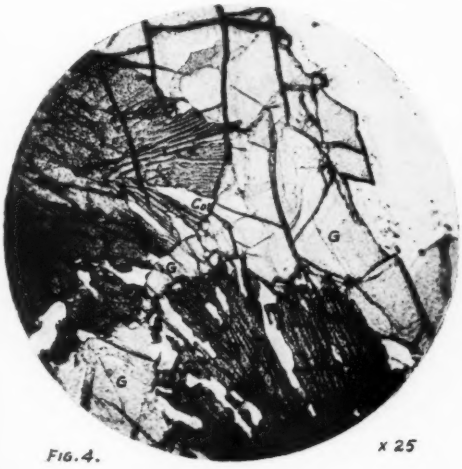


FIG. 4. x 25

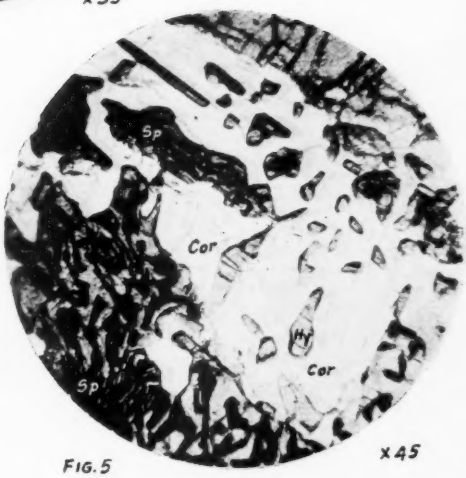


FIG. 5 x 45

It was very kind of him to have arranged for the chemical analysis in his laboratory. He also wishes to thank the research scholars of the Department, Messrs. T. M. Mahadevan and R. S. Paramasivam, for kind assistance during the investigation.

References

1. Crookshank, H. .. "Note on Sapphirine in the Vizagapatam District," *Rec. G. S. India*, 1930, **63**, 446–48.
2. Dana, E. S. .. "A System of Mineralogy," John Wiley, 1920, 561.
3. Mertie, Jr., J. B. .. "Nomograms of Optic Axial Angle Formulæ," *Am. Mineral.*, 1942, **27**, 538–51.
4. Mountain, E. D. .. "Sapphirine Crystals from Blinkwater, Transvaal," *Miner. Mag.*, 1939, **25**, No. 164, 277–82.
5. Prider, R. T. .. "Sapphirine-bearing rocks from Dangin, W. Australia," *Geol. Mag.*, 1945, **82**, 49–54.
6. Walker, T. L., and Collins, W. H. .. "Petrological studies of some rocks from the hill tracts, Vizag Dt.," *Rec. G. S., India*, 1907, **36**, 1–18.
7. Warren, C. H. .. "Ilmenite Rocks near St. Urbain, Quebec ; a New Occurrence of Rutile and Sapphirine," *Am. Jour. Sci.*, 1912, **33**, 263–77.
8. Winchell, A. N. .. "Elements of Optical Mineralogy," John Wiley, 1945, **2**, 427.

Micro-Photographs

Fig. 1. Sapphirine (*Sa*) shows numerous irregular cracks, without any recognizable cleavage. The other minerals are hypersthene (*Hy*) and biotite (*Bi*).

Fig. 2. Idiomorphic sapphirine (*Sa*) and hypersthene (*Hy*) are observed shooting into biotite (*Bi*). Also, sapphirine (*Sa.*) and biotite (*Bi*) occur as patches in hypersthene (*Hy*).

Fig. 3. Intergrowth of sapphirine (*Sa.*) and cordierite (*Cor*).

Fig. 4. Symplektites of hypersthene (*Hy*) and spinel (*Sp*) are truncated by idioblastic garnet (*G*). Cordierite (*Cor*) occurs in elongated narrow irregular stripes in the symplektites ; the three minerals show a general parallelism in their growth.

Fig. 5. Intergrowth of hypersthene (*Hy*) and spinel (*Sp*) with blebs and needles of hypersthene (*Hy*) in a base of cordierite (*Cor*).

ELASTIC CONSTANTS OF SODIUM THIOSULPHATE

By R. V. G. Sundara Rao

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

Received September 27, 1949

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

In the monoclinic system, the complete set of elastic constants has so far been determined only for one crystal, namely potassium dihydrogen tartrate (DKT) by Mason (1946). Since single crystals of fairly large size of sodium thiosulphate pentahydrate, $Na_2S_2O_3\,5H_2O$, or photographer's hypo could be readily grown, it was proposed to determine the elastic constants of the same using the well-known ultrasonic method. The results obtained therefrom are given in the following sections.

Sodium thiosulphate crystallizes in the holohedral monoclinic form having the symmetry C_{2h} with well-developed '*b*' and '*c*' faces. The relevant crystallographic data necessary for identifying the faces and for determining the direction cosines of the normals to some of the faces are given by Groth as follows:—The crystallographic '*b*' axis is perpendicular to the plane containing the '*a*' and '*c*' axes which make an angle β equal to 103° 58′. It has well-developed forms *m* [110], *n* [120], *c* [001] and *q* [011] with the angles between the various faces given below:—

$$m:m = (110):(1\bar{1}0) = 37°\ 36'$$
$$n:b = (120):(010) = 55°\ 45'$$
$$q:b = (011):(010) = 75°\ 5'$$
$$m:c = (110):(001) = 76°\ 48'$$
$$q:n = (011):(120) = 70°\ 17'$$

The axial ratios are as $a:b:c = 0{\cdot}3508:1:0{\cdot}2745$ and the crystal grows most rapidly along the shortest or the '*c*' axis.

2. Elastic Constants of the Monoclinic System

For the purpose of elasticity, the crystal is referred to a set of orthogonal axes X_1, X_2, X_3. In the following procedure, Voigt's convention for the axes is adopted. The positive directions of '*a*' and '*c*' are those that proceed outwards from the obtuse angle β, while the positive direction of '*b*' is such as to make it a right-handed system. The X_1 axis, according to Voigt, coincides with '*c*' in direction and sign and the X_3 axis with '*b*'. The X_2 axis then completes a right-handed orthogonal system thus making an acute angle with the '*a*' axis.

Referring the crystal to such a system of axes, there are thirteen independent constants, *viz.*, C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, C_{23}, C_{16}, C_{26}, C_{36} and C_{45}. To get all the constants, various cuts with their normals oriented in different directions shoud be used. If l, m, n are the direction cosines of the normal identical with X_3' axis, then the constant for the compressional thickness vibration used is

$$\begin{aligned} C_{33}' = {} & l^4C_{11} + m^4C_{22} + n^4C_{33} + m^2n^2\,(4C_{44} + 2C_{23}) \\ & + n^2l^2\,(4C_{55} + 2C_{13}) + l^2m^2\,(4C_{66} + 2C_{12}) \\ & + 4lm\,(l^2C_{16} + m^2C_{26}) + 4lmn^2\,(C_{36} + 2C_{45}) \end{aligned} \qquad (1)$$

The formulæ used for thickness shear vibrations are given by C_{44}' and C_{55}' which can be easily computed for the simple axial cut plates. For a rotation of the normal about X_3 axis, it can be shown that

$$\left.\begin{aligned} C_{44}' = {} & C^2S^2\,(C_{11} - 2C_{12} + C_{22}) - 2CS\,(C^2 - S^2)\,(C_{16} - C_{26}) \\ & + (C^2 - S^2)^2\,C_{66} \\ C_{55}' = {} & S^2C_{44} + C^2C_{55} + 2CS\,C_{45}, \end{aligned}\right\} \qquad (2)$$

where $C = \cos\theta$; $S = \sin\theta$; θ being the angle between X_1 and the normal.

Using the compressional thickness and thickness shear modes of nine suitably cut plates the various constants could be evaluated. The direction cosines of their normals, and the appropriate constants of each plate are given in Table I.

TABLE I

Description & plate No.	Direction cosines of the normal to plates			Effective elastic constant	
	l	m	n	Longitudinal	Torsional
1 X_1-cut	1	0	0	C_{11}	C_{55} & C_{66}
2 X_2-cut	0	1	0	C_{22}	C_{66} & C_{44}
3 X_3-cut	0	0	1	C_{33}	..
4 X_145X_1	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{4}(C_{11}+2C_{12}+C_{22}+4C_{16}+4C_{26}+4C_{66})$	$\frac{1}{4}(C_{11}-2C_{12}+C_{22})$ & $\frac{1}{4}(2C_{44}+2C_{55}+4C_{45})$
5 X_3135X_1	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{4}(C_{11}+2C_{12}+C_{22}-4C_{16}-4C_{26}+4C_{66})$	..
6 X_330X_1	$\frac{\sqrt{3}}{2}$	$\frac{1}{2}$	0	$\frac{1}{16}(9C_{11}+6C_{12}+C_{22}+12\sqrt{3}C_{16}+4\sqrt{3}C_{26}+12C_{66})$	..
7 n-face	0	cos 34° 15′	cos 55° 45′	$m^4C_{22}+n^4C_{33}+2m^2n^2(C_{23}+2C_{44})$	..
8 X_260X_y	$\frac{\sqrt{3}}{2}$	0	$\frac{1}{2}$	$\frac{1}{16}(9C_{11}+2C_{13}+C_{33}+12C_{55})$	..
9 —	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{9}(C_{11}+C_{22}+C_{33})+\frac{2}{9}(C_{12}+C_{13}+C_{23})$ $+\frac{4}{9}(C_{44}+C_{55}+C_{66}+C_{16}+C_{26})+\frac{2}{9}(C_{36}+2C_{45})$	..
10 φ-face	·9376	·2337	·2575	see equation (1)	..

Plate No. 4 for which $1 = m = \frac{1}{\sqrt{2}}$, $n = 0$ has two torsional modes C_{44}' and C_{55}'. It is not possible to identify them individually with the expressions for the two frequencies. C_{44}' and C_{55}' should be determined separately and their values to be added and then equated thus:—

$$C_{44}' + C_{55}' = \tfrac{1}{4}(C_{11} + C_{22} - 2C_{12} + 2C_{44} + 2C_{55} + 4C_{45}) \qquad (3)$$

C_{45} which is the only unknown constant in this equation could be evaluated. Knowing C_{45}, C_{36} could be evaluated from the frequency of longitudinal mode of plate No. 9.

In the actual experiment 10 plates have been used although nine would have been sufficient. Some of the plates have been duplicated. The tenth plate was used for verification. Whenever possible, the natural faces of the crystal have been used in order to avoid errors of orientation in cutting.

For oblique cuts, Cady's notation* is adopted. Thus $X_3 45 X_1$ means that the normal to the section is perpendicular to X_3 and inclined at 45° to X_1. Wherever there are blanks in the torsional column in Table I, it means that only the longitudinal modes need be determined for these plates.

3. Experimental Technique

Single crystals of $2{\cdot}5'' \times 2{\cdot}0'' \times 1{\cdot}0''$ sizes were grown from aqueous solution of hypo. With the help of the crystallographic data, the faces and the axes were determined and subsequently verified by examination under crossed polaroids, using the optical data provided by Groth.

Each section is cut and ground to uniform thickness and worked immediately since otherwise it gets moist and attains the peculiar oily coating observed with hypo crystals. This is probably due to its slowly losing the water of crystallisation. During the experiment also, care was taken to see that the oscillator was not run continuously for more than a short period of 3 to 5 minutes. Otherwise, the crystal gets heated and loses its water. When this happens, the plate changes its thickness enormously, increasing or decreasing depending on the direction of its normal. If this happened the plate is discarded. But if the oscillator does not run continuously, such things happen but rarely. The plates that have been successfully worked did not change their thickness to any appreciable measure and if there is any variation, it is less than ·01 mm. It is of interest to point out that Section 4 in Table I remains practically unaltered in thickness even if considerable heating takes place. In passing, it might be mentioned that the crystals are highly strain- and heat-sensitive.

* *Piezo-electricity*, W. G. Cady.

Tourmaline plates are avoided because the heating effect with them is considerably greater than with quartz plates. X-cut quartz plates for longitudinal and Y-cut plates for torsional modes have been used. Frequencies varying from ·5 to 10 Mc/sec. have been used.

The density of the crystal has been determined using double distilled toluene and is found to be 1·7499 gm./cm.^{3}

4. Experimental Results

The experimental results with the different plates are given in Table II. Sometimes more than one plate of the same type but of different thicknesses have been worked, especially when it is felt that the thickness varied beyond an allowable measure. Those are also recorded in the table.

All the constants are given in units of 10^{11} dynes per sq. cm. In Table II, (l) denotes the longitudinal mode and (t) the torsional mode.

Table II

Plate type No.	Thickness in mm.	Mode	Frequency in Mc /sec.	Effective elastic constant
1	1·45	(l)	1·762	4·569
1	,,	(t)	0·8633	1·096
1	,,	(t)	0·615	0·5568
2	1·61	(l)	1·36	3·355
2	,,	(t)	0·7867	1·123
2	,,	(t)	0·574	0·5977
2	1·66	(l)	1·2896	3·258
3	1·47	(l)	1·412	3·015
4	1·33	(l)	1·695	3·555
4	,,	(t)	0·9217	1·05
4	,,	(t)	0·5009	0·3101
5	1·358	(l)	1·855	4·444
6	1·57	(l)	1·414	3·449
7	1·51	(l)	1·41	3·173
8	1·75	(l)	1·327	3·775
9	1·66	(l)	1·335	3·443
10	1·50	(l)	1·553	3·797

From Tables I and II, the values of C's have been calculated and are given below in units of 10^{11} dynes cm.$^{-2}$

$C_{11} = 4·57$ $C_{44} = 0·60$ $C_{12} = 1·84$ $C_{16} = -0·69$

$C_{22} = 3·31$ $C_{55} = 0·57$ $C_{13} = 1·68$ $C_{26} = +0·25$

$C_{33} = 3·02$ $C_{66} = 1·11$ $C_{23} = 1·83$ $C_{36} = +1·04$

$C_{45} = -0·27$

From these values of C's the elastic moduli s's are calculated. The expressions for converting the C-matrix into the s-matrix are easily derived from the fact that if σ_{ij} is the cofactor of C_{ij} in the C-matrix, then

$$s_{ij} = \frac{\sigma_{ij}}{\Delta}, \tag{3}$$

where Δ is given by the determinant

$$\Delta = \begin{vmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{22} & C_{23} & 0 & 0 & C_{26} \\ C_{13} & C_{23} & C_{33} & 0 & 0 & C_{36} \\ 0 & 0 & 0 & C_{44} & C_{45} & 0 \\ 0 & 0 & 0 & C_{45} & C_{55} & 0 \\ C_{16} & C_{26} & C_{36} & 0 & 0 & C_{66} \end{vmatrix}$$

Because of the presence of a number of zeros, however, the expressions for s_{ij} simplify considerably; and the results are given below:

$$\text{Let } \delta = \begin{vmatrix} C_{11} & C_{12} & C_{13} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{36} \\ C_{16} & C_{26} & C_{36} & C_{66} \end{vmatrix} \quad \text{and } D = \begin{vmatrix} C_{44} & C_{45} \\ C_{45} & C_{55} \end{vmatrix}$$

Then all the s's except s_{44}, s_{45}, s_{55} are given by

$$s_{ij} = (-1)^{i+j} \cdot \frac{\delta_{ij}}{\delta}, \tag{4a}$$

where δ_{ij} is the minor in δ, got by suppressing the ith row and jth column; and the remaining are given by

$$s_{44} = \frac{C_{55}}{D}; \; s_{45} = -\frac{C_{45}}{D}; \; s_{55} = \frac{C_{44}}{D} \tag{4b}$$

Using the expressions (4) the s's were calculated and given below in units of 10^{-13} cm.^{2} dyne^{-1}.

$$\begin{array}{llll} s_{11} = 67{\cdot}4 & s_{44} = 212{\cdot}0 & s_{12} = -6{\cdot}21 & s_{16} = +110{\cdot}0 \\ s_{22} = 50{\cdot}2 & s_{55} = 223{\cdot}0 & s_{13} = -71{\cdot}9 & s_{26} = +15{\cdot}2 \\ s_{33} = 156{\cdot}0 & s_{66} = 327{\cdot}0 & s_{23} = -32{\cdot}3 & s_{36} = -182{\cdot}0 \end{array}$$

$$s_{45} = +100{\cdot}0$$

The linear compressibilities β_1, β_2, β_3 along the three axes X_1, X_2 and X_3 and the cubic compressibility $\beta = \beta_1 + \beta_2 + \beta_3$ are also calculated from expressions of the type

$$\beta_i = s_{i1} + s_{i2} + s_{i3} \qquad (i = 1, 2, 3) \tag{5}$$

and in the above units they are

$$\beta_1 = -10{\cdot}7 \qquad \beta_2 = 11{\cdot}7 \qquad \beta_3 = 52{\cdot}0 \qquad \beta = 53{\cdot}0.$$

In the literature no data concerning sodium thiosulphate are available.

The author thanks Prof. R. S. Krishnan for his kind interest and encouragement in the investigation. He also thanks Miss C. Shantakumari for the loan of the crystals.

5. Summary

The thirteen elastic constants of " hypo " or sodium thiosulphate have been determined by the ultrasonic method. They are in units of 10^{11} dynes cm.$^{-2}$

$C_{11} = 4{\cdot}57$	$C_{44} = 0{\cdot}60$	$C_{12} = 1{\cdot}84$	$C_{16} = -0{\cdot}69$
$C_{22} = 3{\cdot}31$	$C_{55} = 0{\cdot}57$	$C_{13} = 1{\cdot}68$	$C_{26} = +0{\cdot}25$
$C_{33} = 3{\cdot}02$	$C_{66} = 1{\cdot}11$	$C_{23} = 1{\cdot}83$	$C_{36} = +1{\cdot}04$

$$C_{45} = -0{\cdot}27$$

The corresponding s's have also been calculated.

References

Groth, P. .. *Chem. Krystallographie*, **2**.

Mason, W. P. .. *Phy. Rev.*, 1946, **70**, 705.

COMPARISON OF THE INFRA-RED ACTIVITIES OF THE FOUR RAMAN-INACTIVE VIBRATIONS IN α–QUARTZ

By Bishambhar Dayal Saksena and Shanti Swarup Bhatnagar

(Department of Physics, University of Allahabad, Allahabad, India)

Received September 29, 1949

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The modes of vibration of α-quartz have been analysed by one of us (Saksena, 1940). The unit cell of α-quartz contains six silicon and six oxygen atoms, each silicon atom being shared between two cells. This corresponds to the molecular formula $3\,SiO_2$. There are 27 modes of vibration of this group of which three are translational and the remaining 24 are internal modes. As α-quartz belongs to the point-group D_3, these modes are divided into three classes A, B and E, of which A is totally symmetric, B anti-symmetric and E doubly degenerate. The 24 modes are divided as follows—namely 4 in class A, 4 in class B, and 8 in class E. Class A is active in Raman effect only, class B in infra-red only and class E in both. For class B, the change of electric moment occurs only along the optic axis of the crystal which is taken as the z-axis, the other two, namely the electrical and mechanical axes, being called the x-axis and y-axis respectively. From the reflection experiments of Rubens, Reinkobar and others, reference to whose work may be found in the paper mentioned above, Saksena took the frequencies falling in class B as 1149 ($8{\cdot}7\,\mu$), 777 ($12{\cdot}87\,\mu$), 508 ($19{\cdot}7\,\mu$), 364 ($27{\cdot}5\,\mu$). The percentage of reflection is 90 for $19{\cdot}7\,\mu$, 88 for $8{\cdot}7\,\mu$, 67 for $27{\cdot}5\,\mu$ and 40 for $12{\cdot}87\,\mu$. If the percentage of reflection be supposed to represent the intensities of these vibrations it would appear that $19{\cdot}7\,\mu$ and $8{\cdot}7\,\mu$ are the strongest and very nearly of the same intensity, next in order is $27{\cdot}5\,\mu$ and the weakest is $12{\cdot}87\,\mu$. There is no data for the intensities of these frequencies in absorption but as the maxima in reflection generally agree with those in absorption, the above will also represent the intensities in absorption.

The intensity of a fundamental ν_i in absorption is proportional to $\nu_i\left(\frac{dM}{d\xi}\right)^2$ (Herzberg, 1943) where $\frac{dM}{d\xi}$ represents the change in dipole moment with the normal mode of vibration ξ. To a first approximation the changes of dipole moment produced by the displacement of atoms of a molecule in a given normal mode may be associated with the stretching

and bending of individual bonds and the effect may be summed up for all the bonds in the molecule. Wolkenstein (1945) has shown that the principle of additive bond contribution is in accord with the qualitative data of absorption intensities in a number of simple cases. In the case of bending vibrations there is no change in the bond moment as the bond distances remain practically unaltered. The change of dipole moment during the vibration can be calculated directly from the bond moments and displacement of atoms. Bell (1948) has in this way found the moment of C–H bond from the intensities of the C–H bending vibrations. In the case of stretching vibrations there is no agreed theoretical basis for calculating the changes of dipole moment. Rollefson and Havens (1940) consider it highly probable that the charge on an atom is not constant during a vibration.

In calculating the piezo-electric constants of α-quartz (Saksena, 1948), it was supposed that during an elastic deformation the electric moment arises from a change of bond distances and bond angles on strain. It should be justifiable to make a similar assumption in calculating the electric moment during the infra-red vibration, for both the processes, namely the elastic deformation and infra-red vibration, take place sufficiently slowly for the electron cloud to adjust itself to changed conditions. Saksena (1944) has calculated the elastic constants and the infra-red frequencies of α-quartz by using the same force constants. The observations made in the preceding paragraph lend additional support to this view because the Si–O bonds in quartz are largely covalent in nature. In this paper we have compared the intensities of the four infra-red active modes of class B of α-quartz. We have no data on the absolute intensities of the four vibrations, namely $8{\cdot}7\,\mu$, $12{\cdot}87\,\mu$, $19{\cdot}7\,\mu$ and $27{\cdot}5\,\mu$, but qualitatively the observed and the calculated intensities are in good agreement.

2. Method

There are six silicon and six oxygen atoms in the unit cell of α-quartz. Each silicon atom is linked to four oxygens and each oxygen has two silicon atoms as near neighbours. Thus at each silicon atom there are four Si–O bonds but as each silicon is linked to two cells there are twelve Si–O bonds in each unit cell. There are also just 12 positive and 12 negative charges, as each silicon carries a charge of $+4$ units and each oxygen a charge of -2 units. Each Si–O bond may therefore represent a sharing of charge $k.e$ units where k is in the neighbourhood of unity. If all the bonds be treated as equivalent, each will have the same value k, otherwise, due to symmetry, six of them will have a value k_1, and the other six a value k_2. We may now calculate the moment produced by the stretching and bending of a bond.

A change of length Δr along the bond direction would give a moment $ke.\,\Delta r$ in that direction. The electric moment is directed from the silicon to the oxygen atom so that a negative value of Δr gives a moment opposite in direction. If a Si–O bond of length r is displaced from its original position by an angle $\Delta\theta$ such that the oxygen has moved a distance $r.\,\Delta\theta$, the moment produced at right angles to the bond direction is $ker.\,\Delta\theta$. This is the moment due to bending of the bond and it may be put as $ke\,(\delta_0 - \delta_{si})$, where δ_0 and δ_{si} represent the displacements of oxygen and silicon atoms. The direction of this moment, which is normal to the Si–O bond, is such that there is a transport of negative charge due to the motion of the oxygen atom away from the silicon atom. The electric moment therefore appears in the direction leading from oxygen to silicon atom normal to the bond. If x_1, y_1, z_1 are the co-ordinates of the silicon atom and x_2, y_2, z_2 of the oxygen atom and if $x_1+\Delta x_1$, $y_1+\Delta y_1$, $z_1+\Delta z_1$, and $x_2+\Delta x_2$, $y_2+\Delta y_2$, $z_2+\Delta z_2$, represent their displaced positions then since

$$\delta_{si} = \sqrt{\Delta x_1^2 + \Delta y_1^2 + \Delta z_1^2}$$

and

$$\delta_0 = \sqrt{\Delta x_2^2 + \Delta y_2^2 + \Delta z_2^2}$$

the resolved parts of the bending moments along the axis of the crystal are $ke\,(\Delta x_2 - \Delta x_1)$, $ke\,(\Delta y_2 - \Delta y_1)$, and $ke\,(\Delta z_2 - \Delta z_1)$ in a direction pointing from oxygen to silicon atom. Bell has used an equivalent expression

$$\mu_e = \mu_{CH}\,\Sigma\,(x_H - x_C),$$

where μ_e is the effective moment for infra-red absorption, μ_{CH} the moment of the C–H bond and x is the displacement of the given atom.

For finding the resultant moment we have to sum up the resolved parts of the stretching and the bending moments due to all the bonds in the unit cell. It is shown in a later section that the resolved parts of both the stretching and bending moments along the x and y directions of the crystal are zero. The net moment arises only along the optic axis.

3. Normal Modes of Vibration

In order to find the displacements of atoms we shall first obtain the normal modes of vibrations. The displacements of atoms in any given mode ν may be found out by equating the maximum value of the potential energy of the unit cell for the given mode equal to $h\nu$.

The frequencies of the four modes falling in class B have been calculated by Saksena in an earlier paper (Saksena, 1945). It was shown that if α, β, γ, δ are the displacements in the four symmetry modes

$A \rightarrow m_0^{\frac{1}{2}}(z_1 + z_2 + z_3 + z_4 + z_5 + z_6) - m_{Si}^{\frac{1}{2}}(z_7 + z_8 + z_9 + z_{10} + z_{11} + z_{12})$

$B \rightarrow \quad y_2 + y_4 + y_6 - y_1 - y_3 - y_5$

$C \rightarrow \quad y_8 + y_{10} + y_{12} + y_7 + y_9 + y_{11}$

$D \rightarrow \quad x_7 + x_9 + x_{11} - x_8 - x_{10} - x_{12}$

where the numbers 1 to 6 represent silicon atoms and 7 to 12 oxygen atoms and x, y, z have their usual significance, the potential energy is given by $2V = 6(a\delta^2 + b\gamma^2 + c\beta^2 + d\alpha^2 + 2e\delta\gamma + 2f\delta\beta + 2g\delta\alpha + 2h\gamma\beta + 2i\gamma\alpha + 2j\alpha\beta)$ and the kinetic energy by

$$2T = 6(16\dot{\delta}^2 + 16\dot{\gamma}^2 + 14{\cdot}15\dot{\beta}^2 + 36{\cdot}3\dot{\alpha}^2)$$

and we have then

$$\left.\begin{aligned} &(a - 16\lambda^2)\delta + e\gamma + f\beta + g\alpha = 0 \\ &e\delta + (b - 16\lambda^2)\gamma + h\beta + i\alpha = 0 \\ &f\delta + h\gamma + (c - 14{\cdot}15\lambda^2)\beta + j\alpha = 0 \\ &g\delta + i\gamma + j\beta + (d - 36{\cdot}3\lambda^2)\alpha = 0. \end{aligned}\right\} \quad (1)$$

The frequencies are given by the determinant

$$\begin{vmatrix} (a - 16\lambda^2) & e & f & g \\ e & (b - 16\lambda^2) & h & i \\ f & h & (c - 14{\cdot}15\lambda^2) & j \\ g & i & j & (d - 36{\cdot}3\lambda^2) \end{vmatrix} = 0 \quad (2)$$

If $\Delta_1, \Delta_2, \Delta_3, \Delta_4$ are the minors of this determinant the last three equations of (1) give

$$\frac{\delta}{\Delta_1} = \frac{-\gamma}{\Delta_2} = \frac{\beta}{\Delta_3} = \frac{-\alpha}{\Delta_4}. \quad (3)$$

Using $k = 5{\cdot}01 \times 10^5$ dynes, $k_1 = 1{\cdot}056 \times 10^{-11}$ dynes,

$k_2 = 1{\cdot}315 \times 10^{-11}$ dynes, $k_3 = -{\cdot}8992 \times 10^5$ dynes,

we get

$$\begin{aligned} \Delta_1 &= -8218{\cdot}32\,\lambda^6 + 10343{\cdot}5206\,\lambda^4 - 3534{\cdot}523\,\lambda^2 + 300{\cdot}5203 \\ \Delta_2 &= \quad 330{\cdot}4278\,\lambda^4 - 17{\cdot}8368\,\lambda^2 - 43{\cdot}8367 \\ \Delta_3 &= -660{\cdot}1373\,\lambda^4 + 482{\cdot}5524\,\lambda^2 - 60{\cdot}8692 \\ \Delta_4 &= -843{\cdot}3173\,\lambda^4 + 452{\cdot}0957\,\lambda^2 - 54{\cdot}8316 \end{aligned}$$

The frequencies calculated with the above force constants are 1160, 809, 489, 149.

The values of $\Delta_1, \Delta_2, \Delta_3, \Delta_4$ for various frequencies are given by:

TABLE I

Frequency	λ^2	Δ_1	Δ_2	Δ_3	Δ_4
1160	·7889	−85·4664	147·6901	−90·9871	−222·9697
809	·3833	2·3943	− 2·1607	27·1189	− 5·4266
489	·1403	−11·8003	−40·0419	− 6·8744	− 8·5191
149	·01096	263·0134	−44·0195	−55·6597	− 49·9779

The four normal modes are given by

$$\left(\frac{36\cdot3}{16}\right)^{\frac{1}{2}}\alpha_i A + \left(\frac{14\cdot15}{16}\right)^{\frac{1}{2}}\beta_i B + \gamma_i C + \delta_i D \qquad [i = 1, 2, 3, 4]$$

As the modes are orthogonal, they satisfy the relations of the type

$$\frac{36\cdot3}{16}\alpha_1\alpha_2 + \frac{14\cdot15}{16}\beta_1\beta_2 + \gamma_1\gamma_2 + \delta_1\delta_2 = 0.$$

Using (3) the normal mode may also be written as

$$-(36\cdot3)^{\frac{1}{2}}\frac{\Delta_4}{\Delta_1}A + (14\cdot15)^{\frac{1}{2}}\frac{\Delta_3}{\Delta_1}B - (16)^{\frac{1}{2}}\frac{\Delta_2 C}{\Delta_1} + (16)^{\frac{1}{2}}D$$

4. DISPLACEMENTS OF ATOMS

It may be seen that each normal mode is a linear combination of the four symmetry modes with different amplitudes and different masses. As may be seen from the expressions of kinetic energy, $6 \times 36\cdot3$, $6 \times 14\cdot15$, 6×16, 6×16, are the effective oscillating masses in the four modes. The remaining term gives the amplitude. Thus if δ be the amplitude in the symmetry mode D, $-\frac{\Delta_2}{\Delta_1}\delta$ is the amplitude in the mode C, $\frac{\Delta_3}{\Delta_1}\delta$ is the amplitude in the mode B and $-\frac{\Delta_4}{\Delta_1}\delta$ in the mode A. To calculate the value of δ for each frequency we take the maximum value of the potential energy as $h\nu$ and with the help of (3) calculate δ. The results in units of $(10)^{-10}$ cm. are shown in Table II.

TABLE II

Frequency	α	β	γ	δ	$\Delta r_{1,7}$	$\Delta r_{2,7}$
1160	−1·422	·5805	·9426	·5455	−2·533	2·6804
809	·5948	2·972	·2368	·2623	−2·024	−1·867
489	− ·7391	·5965	−3·474	1·024	1·992	− ·676
149	1·332	−1·484	1·174	7·013	·4268	1·846

The displacement of atoms for various frequencies may be calculated from the four symmetry modes. The displacement along the co-ordinate axes are given in Table III.

TABLE III

Atom	x	y	z
1–Si ..	0	β	$\frac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
7–O ..	$-\frac{1\cdot4386}{1\cdot882}\delta+\frac{1\cdot214}{1\cdot882}\gamma$	$-\frac{1\cdot214}{1\cdot882}\delta-\frac{1\cdot4386}{1\cdot882}\gamma$	$-\frac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
2–Si ..	$\frac{\sqrt{3}}{2}\beta$	$-\frac{\beta}{2}$	$\frac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
8–O ..	$\frac{\cdot3322}{1\cdot882}\delta+\frac{1\cdot853}{1\cdot882}\gamma$	$\frac{1\cdot853}{1\cdot882}\delta-\frac{\cdot3322}{1\cdot882}\gamma$	$-\frac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
3–Si ..	$-\frac{\sqrt{3}}{2}\beta$	$-\frac{\beta}{2}$	$\frac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
9–O ..	$\frac{1\cdot7708}{1\cdot882}\delta+\frac{\cdot6389}{1\cdot882}\gamma$	$-\frac{\cdot6389}{1\cdot882}\delta+\frac{1\cdot7708}{1\cdot882}\gamma$	$-\frac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
4–Si ..	0	β	$\frac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
10–O ..	$-\frac{1\cdot7708}{1\cdot882}\delta-\frac{\cdot6389}{1\cdot882}\gamma$	$-\frac{\cdot6389}{1\cdot882}\delta+\frac{1\cdot7708}{1\cdot882}\gamma$	$-\frac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
5–Si ..	$\frac{\sqrt{3}}{2}\beta$	$-\frac{\beta}{2}$	$\frac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
11–O .	$-\frac{\cdot3322}{1\cdot882}\delta-\frac{1\cdot853}{1\cdot882}\gamma$	$\frac{1\cdot853}{1\cdot882}\delta-\frac{\cdot3322}{1\cdot882}\gamma$	$-\frac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
6–Si ..	$-\frac{\sqrt{3}}{2}\beta$	$-\frac{\beta}{2}$	$\frac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
12–O ..	$\frac{1\cdot4386}{1\cdot882}\delta-\frac{1\cdot214}{1\cdot882}\gamma$	$-\frac{1\cdot214}{1\cdot882}\delta-\frac{1\cdot4386}{1\cdot882}\gamma$	$-\frac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$

The values of α, β, γ, δ are given in Table II.

It may be seen from this table that the sum of the moments due to all the bonds along the x and y direction are zero, *i.e.*,

$$\Sigma_{12}\, ke\,(\delta x_0 - \delta x_{Si}) = 0$$
$$\Sigma_{12}\, ke\,(\delta y_0 - \delta y_{Si}) = 0,$$

where δx and δy are the displacements along the x and y axes of the silicon and oxygen atoms. The moment is only along the z-axis and is directed from oxygen to silicon, *i.e.*, along the positive direction of the optic axis, for according to symmetry mode A the silicon is moving up and the oxygen is moving down along the optic axis. This moment is equal to

$$\alpha \cdot \frac{m_0 + m_{Si}}{m_0^{\frac{1}{2}}\, m_{Si}^{\frac{1}{2}}} = 2{\cdot}082\alpha \text{ per bond.}$$

The total moment is therefore $12\,ke \times 2{\cdot}082\,\alpha$ and is directed along the positive direction of the optic axis, if α is positive. Thus for various frequencies the moments along the positive direction of the optic axis due to bending moment of all the bonds in the unit cell are given by:

Frequency	1160	489	809	149
Moment	$-5{\cdot}92$	$-3{\cdot}077$	$2{\cdot}477$	$5{\cdot}546 \times (6ke \times 10^{-10})$

The change in the bond length can be calculated from the relations,

$$1{\cdot}588\,\Delta r_{1,7} = -\,{\cdot}1672\delta - 1{\cdot}447\gamma - 1{\cdot}214\beta + 1{\cdot}311\alpha$$
$$1{\cdot}588\,\Delta r_{2,7} = {\cdot}5963\delta + {\cdot}8935\gamma - {\cdot}6348\beta - 2{\cdot}431\alpha$$

where $\Delta r_{1,7} = \Delta r_{3,9} = \Delta r_{5,11} = -\Delta r_{1,12} = -\Delta r_{5,10} = -\Delta r_{3,8}$

$$\Delta r_{2,7} = \Delta r_{4,9} = \Delta r_{6,11} = -\Delta r_{2,8} = -\Delta r_{4,10} = -\Delta r_{6,12}.$$

The values of $\Delta r_{1,7}$ and $\Delta r_{2,7}$ have already been calculated in Table II.

As the moments along the bonds are directed from silicon to oxygen the direction cosines of the bonds are given in Table IV. The resolved parts along the axes of the stretching bond moments are then $ke.\Delta r.l$, $ke.\Delta r.m$. $ke.\Delta r.n$.

TABLE IV

d.c.	$r_{2,8}$	$r_{2,7}$	$r_{1,7}$	$r_{1,12}$	$r_{6,12}$	$r_{5,11}$	$r_{5,10}$	$r_{4,10}$	$r_{4,9}$	$r_{3,9}$	$r_{3,8}$	$r_{6,11}$
l ..	$-$ ·9858	$+$·1206	$-$ ·8054	$-$ ·8054	$+$ ·1206	$+1{\cdot}454$	$-$ ·6488	$+$ ·8642	$+$ ·8642	$-$ ·6488	$+1{\cdot}454$	$-$ ·9858
m ..	$-$ ·4290	$-1{\cdot}068$	$+1{\cdot}214$	$-1{\cdot}214$	$+1{\cdot}068$	$+$ ·091	$+$ $1{\cdot}305$	$-$ ·6389	$+$ ·6389	$-1{\cdot}305$	$-$ ·091	$+$ ·4290
n ..	$-1{\cdot}168$	$+1{\cdot}168$	$-$ ·63	$+$ ·63	$-1{\cdot}168$	$-$ ·63	$+$ ·63	$-1{\cdot}168$	$+1{\cdot}168$	$-$ ·63	$+$ ·63	$+1{\cdot}168$

Summing up for all the bonds in the unit cell we see that the resolved parts of the moments along the x and y axes are zero, *i.e.*,

$$\sum^{12} ke.\Delta r.1 = 0$$

$$\sum^{12} ke.\Delta r.m = 0.$$

Along the z-axis the moments are:

Frequency	1160	809	489	149
Moment	2·977	−·57	−1·286	$1{\cdot}19 \times (6ke \times 10^{-10})$

This may be visualised in another way also. The negative value of $\Delta r_{1,7}$ for 1160 gives a moment in the direction 7 to 1, *i.e.*, from oxygen to silicon and as the silicon atom is above the oxygen atom its resolved part along the optic axis is along the positive direction. Similarly the positive value of $\Delta r_{2,7}$ gives a moment from silicon to oxygen, and since silicon atom 2 is below the oxygen the resolved part of this moment is also along the positive direction of the optic axis. The two moments are in the same direction and can therefore be added up.

Summing up the moments due to stretching and bending of bonds we get the total moment and the intensities of the absorption bands along the optic axis. The results for the various frequencies are as follows:

Frequency	1160	809	489	149
$\frac{dM}{d\xi}$ =	−2·943	1·907	−4·363	$6{\cdot}736 \times (6ke \times 10^{-10})$
$I = \nu\left(\frac{dM}{d\xi}\right)^2 \propto$	10	2·9	9·3	6·8

We thus see that the weakest line is 809 and that 1160 and 489 are almost of the same intensity. The results are in agreement with the observed intensities of these frequencies.

6. Summary

The electric moments developed during an infra-red vibration have been calculated by supposing that the moments produced may be divided into two parts, one due to bending of bonds and the other due to the stretching of bonds. By taking the stretching moment as $ke.\Delta r$ acting from silicon to oxygen atom where Δr gives the change in bond length, the moments due to all the bonds can be resolved along the axis. It is found that the resolved parts are zero along the x and y directions. The bending moment is given by $ke\,(\delta_0 - \delta_{Si})$, where δ_{Si} and δ_0 are the displacements of silicon and oxygen

atoms and acts along the direction leading from oxygen to silicon atom normal to the bond. It is again seen by resolving moments along the axes and adding the results for various bonds that the net moment arises only along the optic axis. The two moments then can be added up. It is then seen that the frequencies 1160 and 489 have almost the same intensity and 809 is the weakest.

References

Saksena, B. D. .. *Proc. Ind. Acad. Sci.*, A, 1940, **12**, 93.

——————— .. *Ibid.*, 1944, **19**, 357.

——————— .. *Ibid.*, 1945, **22**, 379.

——————— .. *Ibid.*, 1948, **28**, 423.

Herzberg, G. .. *Raman and Infrared Spectra of Polyatomic Molecules*, 1943, 261.

Wolkenstein .. *Acta Physico-chem., U. R. S. S.*, 1945, **20**, 833.

Bell .. *Proc. Roy. Soc.*, 1948, 192, 498.

Rollefson and Havens .. *Phy. Rev.*, 1940, **57**, 710.

IONIC POLARISATION IN CRYSTALS: ADDITIVITY IN DOUBLE SALTS

By D. A. A. S. Narayana Rao

(From the Department of Physics, Andhra University, Waltair)

Received October 20, 1949

(Communicated by Prof. S. Bhagavantam, F.A.SC.)

1. Introduction

The total molecular polarisation of a substance can be calculated from the formula $P = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho}$, where ϵ is the dielectric constant, M the molecular weight, and ρ the density. This total polarisation is known to be the sum of three quantities, P_E the electronic polarisation, P_A the atomic polarisation (or the ionic polarisation in the case of ionic crystals), and P_O the orientation polarisation associated with polar molecules. It should be noted that the above equation for total polarisation holds good only for gases in which the internal field is given by Clausius-Mossotti considerations. The orientation polarisation in liquids invalidates the Clausius-Mossotti field and so the total polarisation in liquids consisting of polar molecules cannot be calculated from the above expression. But in the case of non-polar liquids, and in the case of solids when the dielectric constant is determined at a high frequency and far from the melting point, the orientation polarisation does not exist. With distortion-polarisation alone, the Clausius-Mossotti formula is established at least as a good approximation and so we can calculate the total polarisation in the above two cases by the expression $\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho}$. This is the sum of the two quantities, electronic and ionic (or atomic) polarisations. The electronic polarisation $\frac{n_\infty^2 - 1}{n_\infty^2 + 2}\frac{M}{\rho}$ can be separately obtained from the refraction data. The refractive indices in the visible region—sufficiently far off from the ultraviolet absorption wave-lengths—are to be extrapolated for infinite wave-length and n_∞ obtained. This may be done using a one term Sellmeier expression or even the simpler formula of Cauchy. The ionic polarisation is given by $\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho} - \frac{n_\infty^2 - 1}{n_\infty^2 + 2}\frac{M}{\rho}$.

Cheng[1] showed that each molecule of water in the compounds $CuSO_4\,5H_2O$, $MgSO_4\,7H_2O$, $ZnSO_4\,7H_2O$ contributes to the total polarisation approximately the same quantity as the molecular polarisation of ice. This means that the total polarisation of the composite molecule follows scalar

additivity with respect to the polarisations of the constituent molecules. Electronic polarisation (or molar refraction) is known to follow scalar additivity and so the work of Cheng contains the implication that the ionic polarisation also follows scalar additivity in these compounds. An attempt is made in this investigation to examine the validity of scalar additivity with respect to the ionic polarisations of compounds containing water of crystallisation and compounds containing double molecules as zircon ($ZrO_2 - SiO_2$), spinel ($MgOAl_2O_3$) and dolomite ($CaCO_3 - MgCO_3$).

2. Results

The refractive indices and densities for the calculations are taken from Landolt and Bornstein's Tables. The dielectric constants in Table I are those reported by Cheng[1] or Heydweiller.[2] The dielectric constants in Table II are those determined by the author[3] or taken from Landolt and Bornstein's Tables.

In the calculation of the mean electronic or total polarisation of crystals which are not of cubic symmetry, the average dielectric constant given by $\frac{\epsilon_1+\epsilon_2+\epsilon_3}{3}$ and the average n_∞ given by $\sqrt{\frac{n_{1\infty}^2+n_{2\infty}^2+n_{3\infty}^2}{3}}$ are used. For substances in which the dielectric constant is determined in the powder form, that value is taken to represent the mean.

Table I

	ρ	ϵ	n_∞^2	P	P_E	P_E'	P_A	P_A'
Ice ..	0·916	3·16	1·635	8·23	3·43		4·8	
$BaCl_2$ ..	3·86	11·4	2·95	41·9	21·3		20·6	
$BaCl_2 2H_2O$ ..	3·10	9·4	2·64	58·0	27·8	28·2	30·2	30·2
Na_2CO_3 ..	2·45	8·4	2·21	30·8	12·4		18·4	
$Na_2CO_3 10H_2O$ ..	1·47	5·3	1·96	114·7	47·2	46·7	67·5	66·4
$MgSO_4$ ..	2·66	8·2	2·34	31·9	13·9		18·0	
$MgSO_4 7H_2O$ ..	1·68	5·91	2·06	91·1	38·3	39·9	52·8	51·6
$CuSO_4 H_2O$ ..	3·15	7·0	2·72	37·6	20·5		17·1	
$CuSO_4 5H_2O$ ..	2·29	6·46	2·31	70·5	33·1	34·2	37·4	36·3

Table II

	ρ	ϵ_1	$\epsilon_2=\epsilon_3$	ϵ (mean)	n_∞^2 (mean)	P	P_E	P_E'	P_A	P_A'
$CaCO_3$ ..	2·75	8·2	8·7	8·53	2·52	26·0	12·2		13·8	
$MgCO_3$ ..	3·04	8·1	6·9	7·30	2·68	18·8	10·0		8·8	
$CaMg(CO_3)_2$ ..	2·83	6·8	7·8	7·47	2·59	44·5	22·6	22·2	21·9	22·6
SiO_2 ..	2·66	4·6	4·45	4·5	2·36	12·1	7·0		5·1	
ZrO_2 .	5·49	..	..	12·4	4·44	17·8	12·0		5·8	
$ZrSiO_4$ ..	4·70	12·85	12·6	12·68	3·63	31·0	18·2	19·0	12·8	10·9
MgO. ..	3·43	8·2	8·2	8·2	2·93	8·3	4·6		3·7	
Al_2O_3 ..	3·82	10·9	9·6	10·03	3·01	20·0	10·7		9·3	
$MgAl_2O_4$ ..	3·58	8·6	8·6	8·6	2·86	28·5	15·2	5·3	13·3	13·0

The ionic polarisations and other data for compounds containing water of crystallisation are given in Table I. Table II contains the ionic polarisations and other data of three double salts and the constituent salts studied in the crystalline form. P_E' and P_A' are the electronic and ionic polarisations of the composite substance obtained by adding up the respective polarisations of the constituent molecules.

3. Discussion of Results

It can be seen from Tables I and II that the electronic as well as the ionic polarisations of the composite salt found directly and calculated by addition from the respective polarisations of the component molecules are nearly the same. The differences are very small except in the case of the ionic polarisation of zircon. The differences may be partly due to the approximate nature of the expression used for the calculation of polarisation which is valid only for crystals of cubic symmetry with non-overlapping ions. The ionic polarisation of the composite salt is in general slightly higher than the sum of the ionic polarisations of the constituent molecules except in the case of dolomite and the electronic polarisation under the same circumstances is slightly lower. It is suggestive of slight changes in the ionic and electronic polarisations of a molecule in opposite directions when it is linked to other molecules into a complex. This mutual influence of the molecules over one another in the complex partly explains the small differences between P_A, P_A' and P_E, P_E'.

4. Summary

The electronic $\frac{n_\infty^2 - 1}{n_\infty^2 + 2}\frac{M}{\rho}$ and the ionic $\left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n_\infty^2 - 1}{n_\infty^2 + 2}\right)\frac{M}{\rho}$ polarisations are calculated for a number of hydrated salts, in the hydrated and anhydrous conditions, for zircon ($ZrO_2\ SiO_2$), spinel ($MgO\ Al_2O_3$) and dolomite [$Ca\ Mg\ (CO_3)_2$] and for the constituent substances of the latter three compounds. It is shown that in all these compounds, the electronic and ionic polarisations are nearly the sums respectively of the electronic and ionic polarisations of the constituent molecules separately considered. The probable reasons for the small departures from additivity are discussed.

The author wishes to express his grateful thanks to Prof. S. Bhagavantam for his keen interest in this work.

References

1. Cheng .. *Phil. Mag.*, 1940, **30**, 505.
2. Heydweiller .. *Zeits. f. Phys.*, 1920, **3**, 308.
3. Narayana Rao .. *Proc. Ind. Acad. Sci.*, A, 1949, **30**, 82.

SOLUBILITY OF SOME SODIUM SOAPS IN PINENE

By Gopal S. Hattiangdi*

(*Chemistry Department, University of Southern California, Los Angeles*)

Received January 2, 1949

(Communicated by Dr. B. Sanjiva Rao, F.A.SC.)

Prasad, Hattiangdi, *et al.* [1, 5, 6, 7] have made extended investigations on the behavior and properties of numerous alkali soap systems in pinene. It is interesting theoretically to correlate the solubility data of soap-solvent systems with their physico-chemical characteristics, and an attempt has been made in this direction in the present paper which deals primarily with the solubility of sodium oleate, stearate and palmitate in pinene, over the temperature range in which the above mentioned authors have measured numerous properties and observed different phenomena.

Earlier references to solubility measurements of soaps in organic solvents are more or less of a qualitative nature. Leggett, Vold and McBain[2] made the first detailed investigations on the solubility of sodium palmitate in nineteen different organic solvents over a wide range of temperatures, and correlated their results with the polarity, internal pressure, spacing, length, etc., of the solvent molecules, as also with the position and nature of the attached groups. More recently, Palit and McBain[4] have conducted extensive measurements on the co-solvency and mix-solvency of several alcohol-hydrocarbon-glycol mixtures for both alkali and heavy metal soaps.

Materials Used

Eastman Kodak pinene was distilled and the middle portion of the distillate, collected at 156° C., was used. The refractive index and specific gravity of the pinene, as determined at 30° C., were 1·4658 and 0·858 respectively.

Sodium oleate and sodium palmitate were products of the British Drug House, and sodium stearate of Messrs. E. Merck & Co. Their melting points as measured by a capillary-type melting point apparatus were 232°, 270° and 260° C. respectively.

Experimental Technique

The procedure adopted for solubility determinations was as follows: About 20 g. of pinene and a slight excess of the dry soap were taken in a

* Present Address : Lever Brothers (India) Limited, Haji Bunder, Sewri, Bombay.

glass-stoppered bottle, and the soap was allowed to swell by keeping the system overnight in an air-thermostat maintained at some constant desired temperature. The soap pinene system was then stirred continuously in a mechanical shaking device for about 6 hours during which interval the solution became saturated with respect to the soap. (Some preliminary experiments showed that equilibrium with respect to saturation was reached within about 4 or 5 hours' shaking, but 6 hours' shaking was considered safe and was therefore adopted in making quantitative estimations). After shaking, the system was allowed to stand at that temperature for a further period of 2 hours after which it was filtered quickly under air pressure through glass-wool in a small fritted glass Buchner funnel. The glass-wool and the whole filtering arrangement were kept at the same temperature as that of the soap-pinene system, thus reducing to a minimum any change in the saturation state.

Pinene reacts fairly vigorously when treated with mineral acids, and hence the chemical method of analysis could not be adopted. The soap content of the solutions was determined as follows: A portion of the filtrate was taken in a shallow weighing bottle, weighed and evaporated carefully to dryness over a sand-bath. It was dried till a constant weight of the white residual soap was obtained. The method was tested with known amounts of soap and pinene, and was found to give results with a reproducibility better than 2 per cent. Care had to be taken while drying the system over the sand-bath to prevent charring of the pinene.

The results obtained are presented in Table I in which the solubility of the soaps in pinene is expressed on a weight-percent basis.

TABLE I

Solubility of some Sodium Soaps in Pinene

Temperature (°C.)	Weight-percent solubility of		
	Sodium palmitate	Sodium stearate	Sodium oleate
30	0·04	0·045	0·05
50	0·25	0·43	0·58
70	0·56	0·85	1·28
90	1·04	1·56	2·17
100	1·57	1·98	2·75
110	1·65	2·10	3·34
120	1·77	2·29	3·37
130	1·94	2·55	3·44
140	2·20	3·01	3·65
150	2·92	..	3·93

Results and their Discussion

The appearance of the soap-pinene systems at various temperatures is interesting. At room temperature and at moderately high temperatures (30° to 50° C.), the soaps do not swell to any appreciable extent. The soap particles exist as semi-fluffy semi-swollen flakes and, in general, do not coalesce to form larger aggregates. The swelling and degree of solvation of the soap particles is considerable at higher temperatures, the undissolved soap existing in the system as a highly swollen gel-like lump. At still higher temperatures, namely above 110° C. the soaps dissolve more freely than at lower temperatures, sodium oleate being the most soluble. If soap-pinene systems are saturated with respect to a high temperature in the abovementioned range and then cooled to about 80° C. or lower, a mixture of clear solution and crystals is not obtained but either a semi-translucent smoky viscous suspension or a very weak and precarious pseudo-gel results.

On cooling the soap-pinene systems of concentrations less than 0·5% the soap sediments out in the form of slightly solvated amorphous or crystalline flakes or as gel-like lumps; the soap, recovered from such systems and dried thoroughly, has the same melting point as that of the original dry soap. At concentrations larger than 0·5%, jellies are obtained which are initially soft and transparent but change over to stiff, translucent or opaque gels on standing. These observations are made at temperatures below 100° C. Above about 110° C. systems of reasonable concentrations (upto about 5% of soap) do not set to jellies or gels even on long standing.

The term "jelly" has been used in the same sense as that suggested by McBain, *et al.*,[3] and signifies a one-phase homogeneous transparent isotropic elastic system. A "gel", on the other hand, is a discontinuous system of two or more components involving a phase of swollen soap, and frequently intermeshed with sol, jelly or liquid crystalline material. Gels are usually opaque or translucent, but can be transparent as a result of suitable combination of the refractive indices of the phases involved. "Pseudo-gels" have a visual appearance resembling that of gels but possess none of their other characteristic properties; according to Prasad, *et al.*,[7] pseudo-gels are systems consisting of a large number of micro-crystallites which enmesh the dispersion medium at random, and have extremely low yield values.

In previous communications to this journal,[1, 5, 6] Prasad, *et al.*, have referred to the "sol-gel" transformation of soap systems in pinene. In actuality, it is a "solution-sol-jelly-gel" transformation, with (*a*) sols and jellies bridging the gap between true molecular solutions and gels, and (*b*) jellies and gels bridging the gap between dry crystalline soaps and their sols in pinene.

It will be seen from the data presented in Table I that the difference in the solubility of sodium palmitate, stearate and oleate is very slight at room temperature and at moderately high temperatures up to about 70° C. At

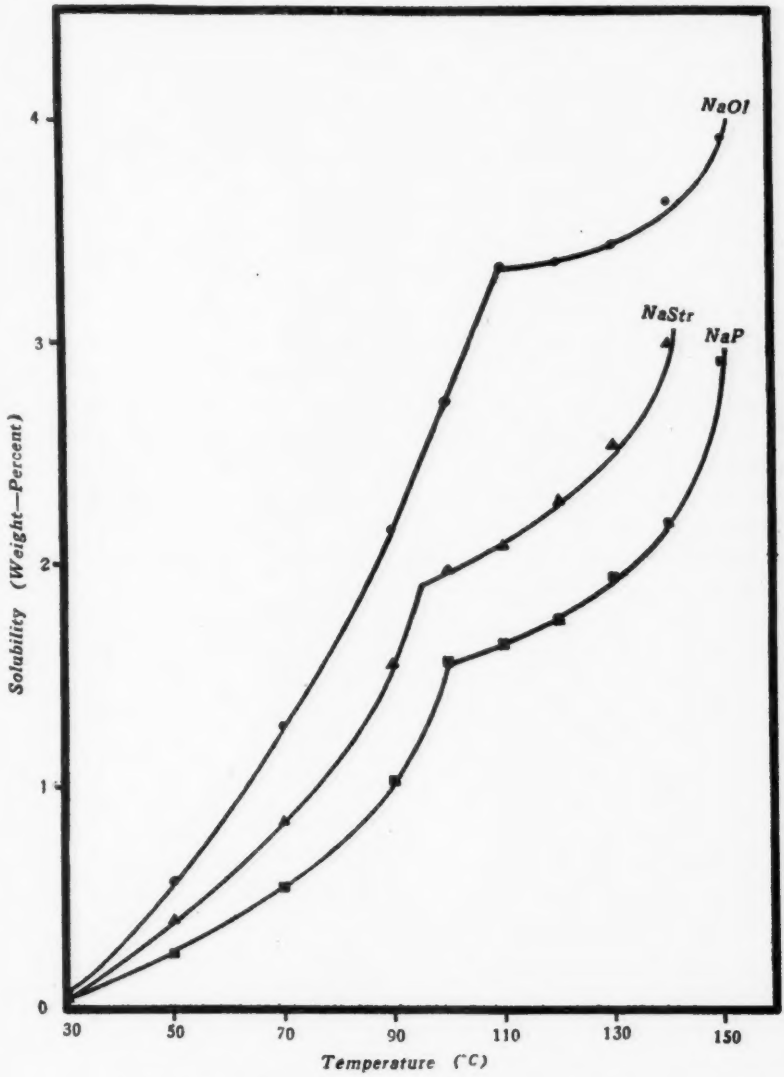


FIG. 1. Solubility Curves of Some Sodium Soaps in Pinene.

elevated temperatures, the solubility of these sodium soaps increases appreciably, being the most for the oleate and the least for the palmitate.

The solubility data when presented graphically as in Fig. 1 shows an interesting point. The solubility curves lie close to the temperature axis initially but shoot upwards after about 70° C. indicating enhanced solubility above this temperature. The solubility increases very slowly in the vicinity of 110° C. and then starts increasing very rapidly as the boiling point of pinene is approached although the absolute solubility remains low. The curves thus show a kink or change in direction nearabouts 100–10°.

These kinks in the solubility temperature curves may be caused by either (*a*) the formation of colloidal micelles, or (*b*) a phase transition of the soap. Prasad, Hattiangdi and Vishvanath[6] have determined the vapour pressures of soap-pinene systems and report that the values of ΔP are measurable within the temperature range 110° to 150° C. below which they are very low. They conclude that the soap-pinene systems exist as true solutions above 110° C. whereas below this temperature aggregation becomes very great and the lowering of vapour pressure is negligible. The close analogy of this observation with the appearance of an elbow or kink in the solubility curves is very interesting and leads one to surmise that the sudden change in solubility is due to saturation and the formation of micelles in the lower temperature range.

The change in the saturation phase, responsible for a change in the direction of the solubility curves, may also be due to a phase transition of the non-solvated soap. The kinks in the solubility curves of sodium palmitate, stearate and oleate in pinene, appear at 100°, 90° and 110° C. respectively, and these temperatures approximate closely to some of the transition temperatures reported by Vold, *et al.*[8] for these soaps in the anhydrous state, namely 114°, 89° and 115° C. The slight deviations in the temperatures at which the actual phase changes take place may be due to either the presence of solvated soap particles in considerably larger amounts of pinene or traces of impurities in the soap sample.

It is possible to construct a partial temperature-composition phase diagram for soap-pinene systems on the basis of the present solubility data and the results reported earlier by Prasad, Hattiangdi, *et al.*[6,7] on the behavior of these same systems. The diagram in Fig. 2 is a generalized schematic representation of the regions of existence of true molecular solutions, colloidal solutions or sols, crystals, pseudo-gels, jellies and gels. It should be noted that the Gibbs' Phase Rule is applicable only to true reversible equilibria such as are found in sols and jellies. Owingto the defective fluidity

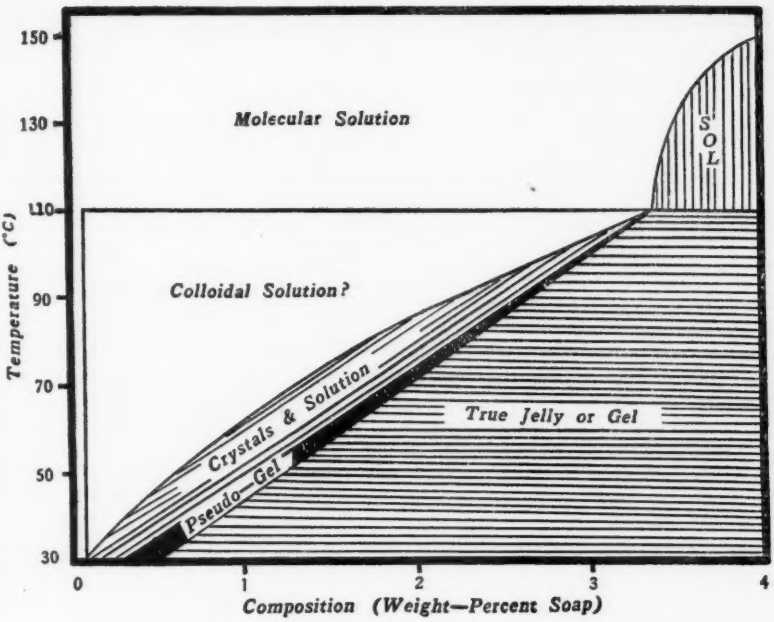


FIG. 2. Schematic Representation of the Regions of Existence of Solutions, Sols, Jellies, Gels, etc., in the system Sodium Oleate—Pinene.

of the liquid crystalline phases, other phases with which they are in equilibrium (such as sol, jelly, crystals and liquid crystals) cannot quite frequently separate or aggregate.

ACKNOWLEDGMENT

The author is very grateful to Professor Robert D. Vold for his keen interest and encouragement during the preparation of this paper.

SUMMARY

1. Solubility curves have been determined over the temperature range 30° to 150° C. for sodium palmitate, stearate and oleate in pinene. The solubility of the three soaps decreases in the order

$$NaOl > NaStr > NaP.$$

2. The solubility curves show a kink or change in direction at about 100° to 110° C. which is caused possibly by either the formation of colloidal micelles or a phase transition of the soap.

3. The regions of existence of solutions, sols, crystals, jellies, gels, etc., in the system sodium oleate-pinene have been indicated in a schematic partial phase diagram.

References

1. Hattiangdi, G. S., *et al.* .. *J. Sci. Ind. Research* (India), 1946, **4,** 489 ; 1947, **6,** 1; *J. Univ. Bombay*, 1945, **14,** 23 ; *Proc. Ind. Acad. Sci.*, 1946, **24**, 295 ; 1947, **27,** 23 ; *Curr. Sci.*, 1947, **16,** 222.
2. Leggett, C. W. Jr., Vold, R. D., and McBain, J. W. *J. Phys. Chem.*, 1940, **44,** 1058 ; 1942, **46,** 429.
3. McBain, J. W., *et al.* .. *J. Phys. Coll. Chem.*, 1947, **51,** 1189 ; *Trans. Farad. Soc.*, 1946, **42 B**, 173.
4. Palit, S. R., and McBain, J. W. .. "*Oil and Soap*," 1946, **23**, 58, 72 ; 1947, **24,** 190 ; *J. Ind. Eng. Chem.*, 1946, **18,** 246, 741.
5. Prasad, M. Hattiangdi, G. S., *et al.* *Proc. Ind. Acad. Sci.*, 1945, **21,** 1, 90, 105 ; 1945, **22,** 320; 1946, **24**, 287.
6. ———, and Vishvanath, C. V. .. *Ibid.*, 1945, **21,** 56.
7. ———, and Wagle, B. K. .. *J. Coll. Sci.*, 1947, **2,** 467.
8. Vold, R. D. .. *J. A. C. S.*, 1941, **63**, 169, 2915.

A NOTE ON THE PREPARATION OF QUINACETOPHENONE

By P. S. Rao and K. L. Gakhar

(Forest Research Institute, Dehra Dun)

Received October 25, 1949

Quinacetophenone was originally prepared by Nencki and Schmid by the interaction of quinol and glacial acetic acid in the presence of fused zinc chloride but the yield was rather poor.[1] Russell and Clark, following the same method, raised the yield to 25 per cent.[2] The ketone was also prepared from quinol diacetate through Fries migration. Contradicting the work of Heller[3] it was shown by Rosenmund and Lohfert[4] that the diesters of quinol do undergo the Fries migration and quinacetophenone was obtained in a yield of 23 per cent. Applying the same reaction, the substance was prepared in more satisfactory yields by Shahane,[5] by Desai and Mavani[6] and very recently by Amin and Shah.[7] The best yield reported so far is that of Shahane, *viz.*, 76 per cent.

For the production of quinacetophenone through Fries reaction, so far only aluminium chloride has been used as the catalyst. It has now been found that using zinc chloride in place of aluminium chloride the ketone can be obtained in almost theoretical yields. The yield is dependent on the duration of treatment and reaches the maximum after 9 hours. Heating beyond this period results in the formation of some inorganic combination of the ketone.

For the preparation of the ketone in best yield, fused zinc chloride (10 g.) was dissolved by heating in glacial acetic acid (10 c.c.) and to this solution was added quinol diacetate (10 g.). The mixture was then mildly boiled under reflux under anhydrous conditions for 9 hours. It was then cooled and treated with 50 per cent. hydrochloric acid (100 c.c.) and left overnight. The deposited solid was then dissolved in 10 per cent. sodium hydroxide (100 c.c.), filtered in order to remove any of the original diacetate, if present, and from the clear alkaline filtrate, on acidification with hydrochloric acid, separated the ketone. The latter was subsequently filtered, washed with cold water and recrystallised from dilute alcohol. The ketone was obtained as colourless narrow rectangular plates melting at 201–02° and the yield

was almost theoretical. Its identity as quinacetophenone was confirmed through its oxime, melting at 149-50°.

References

1. Nencki, M., and Schmid, W. .. *J. prak. Chem.*, 1881, **23**, 546.
2. Russell, A., and Clark, S. F. .. *J. Am. Chem. Soc.*, 1939, **61**, 2654.
3. Heller, G. .. *Ber.*, 1912, **45**, 2389.
4. Rosenmund, K. W., and Lohfert, H. *Ibid.*, 1928, **61**, 2602.
5. Shahane, R. Y. .. *Curr. Sci.*, 1941, **10**, 523.
6. Desai, R. D., and Mavani, C. K. .. *Ibid.*, 1941, **10**, 524.
7. Amin, G. C., and Shah, N. M. .. *J. Ind. Chem. Soc.*, 1948, **25**, 375.

FORMULA OF COMPLEX COMPOUNDS FROM SOLUBILITY DATA

By H. C. Saraswat, M.Sc.

(Department of Chemistry, Christ Church College, Kanpur)

Received August 5, 1949

(Communicated by Dr. K. S. Gururaja Doss, F.A.SC.)

Introduction

Solubility data have been used by A. K. Dey,[1] for calculation of the composition of complex compounds. A mathematical expression has been derived for getting at the formula and its applicability has been shown by calculating the complex formed between the halogens and halides in aqueous solution. It is the object of the present paper to examine critically the formulation given by Dey and to develop a similar formulation for the silver phosphate-ammonia water system studied experimentally in the present work.

Experimental

Preparation of silver phosphate.—Silver ortho-phosphate was obtained by the method of Bury.[2] Solubility of silver phosphate in aqueous ammonia:—Dry stoppered bottles each of capacity 250 c.c. were taken and covered with black paper to eliminate the action of light. 100 c.c. of ammonia solution of strengths—0, 0·004 M, 0·008 M, 0·016 M,.....0·5178 M, was taken in each of the numbered bottles. Freshly prepared silver phosphate was added to each bottle always keeping a large excess of solid silver phosphate. The bottles were then shaken at regular intervals for about six hours. The solutions were filtered and used for estimation of silver phosphate. 25 c.c. of this solution was boiled with excess of nitric acid and the silver nitrate thus obtained was titrated against standard potassium thiocyanate solution. From these data the concentration of silver phosphate in ammonia solutions of different strengths was calculated in millimols per litre. The results are given in Table I.

Table I. *Solubility of Ag_3PO_4 in NH_4OH at 35·5° C.*

Conc. of NH_4OH Millimols/L	Conc. of Ag_3PO_4 Millimols/L	Value of n from graph
0	0	..
4·05	0·133	1
8·09	0·265	1
16·18	0·531	1
32·36	1·061	0·97
64·72	2·057	1
129·45	4·113	1·015
258·90	8·292	1·68
517·80	26·478	..

Discussion

1. *Examination of Dey's formulation.*—Dey considers the reaction $n\mathrm{RX} + \mathrm{X_2} \rightleftharpoons \mathrm{R}_n\,\mathrm{X}_{n+2}$, where X represents a halogen and R represents hydrogen or an alkali metal. By the law of mass action

$$\frac{(\text{complex})}{(\mathrm{RX})^n\,(\mathrm{X_2})} = \mathrm{K}.$$

If b is the solubility of halogen in halide solution of concentration c and a its solubility in water. At the point of equilibrium (complex) $= (b - a)$; $(\mathrm{X_2}) = a$; (RX) used $= (b - a)\,n$; (RX) unused $= c - n\,(b - a)$.

Therefore
$$\frac{(b - a)}{(c - bn + an)^n\,a} = \mathrm{K}$$

and for other corresponding concs, a', b' and c',

$$\frac{(b' - a')}{(c' - b'n + a'n)^n\,a'} = \mathrm{K}$$

If $b - a = s$ and $b' - a' = s'$

$$\frac{s}{(c - sn)^n\,a} = \frac{s'}{(c' - s'n)^n\,a} = \mathrm{K} \text{ as } a = a'$$

or
$$\frac{s}{s'} = \left[\frac{(c - sn)}{(c' - s'n)}\right]^n. \tag{A}$$

Taking logs of both the sides, he gets

$$\log \frac{s}{s'} = n \log \frac{c - sn}{(c' - s'n)} = n\,[\log (c - sn) - \log (c' - s'n)].$$

Expanding the right-hand side in power series and neglecting the second and subsequent terms of the expansion he finally gets

$$\log \frac{s}{s'} = n \log \frac{c}{c'}$$

Therefore
$$n = \frac{\log s/s'}{\log c/c'}$$

$$= \frac{\log (b - a)/(b' - a')}{\log c/c'}. \tag{B}$$

There is slight error in the expansion done by A. K. Dey but as the higher degree terms have been neglected, the final equation is not affected.

The approximation made in deriving the equation (B) from the equation (A) would be permissible only when either the complex formation is weak so that $sn \ll c$ or $n = 1$, in which case s/c equals s'/c'. The success with which Dey could use the equation in halogen-halide system is presumably due to the fact that he is dealing with a system having $n = 1$. He

does get a few large discrepancies and though he attributes this to errors in experimental data, we find by recalculating his values that the larger discrepancies are due to some errors which have presumably crept in his calculations (*vide* Table II).

TABLE II. *KBr + Br_2 system, Dey's Table No. 2*

Kbr	Br_2 dissolved	*n* (Dey)	*n* recalculated
0·	0·43	..	..
0·02	0·47	1·4148	1
0·04	0·51	1·0000	1
0·06	0·55	1·0000	1
0·08	0·59	1·4272	1·43
0·10	0·65	0·9671	0·97
0–20	0·86	0·9658	0·97
0·40	1·27	0·9602	0·96
0·60	1·67	1·0352	1·04
0·80	2·10	1·5118	1·13
0·90	2·335	..	..

In general case wherein the complex formation is considerable and *n* is not equal to unity, the equation (A) would have to be directly used and to solve for *n*, a graphical method may be adopted. This may be done by giving a number of arbitrary values to *n*, in equation $\log s/s' = n \log(c - sn)/(c' - s'n)$ and knowing, *c*, *c'*, *s*, *s'*, from experimental data, the corresponding values of $n \log (c - sn)/(c' - s'n)$ can be obtained. Plotting these values against the arbitrary values of *n*, graphs can be obtained for different sets of values. As $\log s/s'$ is known from the experimental data, its corresponding values of *n*, can be obtained from graph.

Applying this graphical method of calculating *n* to Dey's tables for $KBr + Br_2$ and $KI + I_2$ systems, values of *n* have been obtained. An examination of the values shows that the value is nearly unity invariably showing the formation of KBr_3 and KI_3 respectively. The slight variation in the values seems to be due to some error in calculations as in these particular cases where *n* is unity his approximation is permissible.

2. *The silver phosphate-ammonia water system.*—Coming to the detailed mechanism, the reaction forming the complex may be represented by the following alternative equations:—

(α) $Ag_3PO_4 + m\,NH_3 \rightarrow Ag_2(NH_3)_x\,PO_4^- + Ag(NH_3)_{m-x}$

(β) $Ag_3PO_4 + m\,NH_3 \rightarrow Ag(NH_3)_x\,PO_4^{=} + 2\,Ag(NH_3)_{\frac{m-x}{2}}$

(γ) $Ag_3PO_4 + m\,NH_3 \rightarrow 3\,Ag(NH_3)_{m/3} + PO_4^{\equiv}$

(δ) $Ag_3PO_4 + m NH_3 \rightarrow Ag_3PO_4(NH_3)_m$.

For keeping n, equal to unity, as found by experiment, it would be necessary that m in the above mechanisms should be respectively equal to 2, 3, 4, and 1. Since however it is found that addition of silver phosphate to aqueous ammonia increases the electrolytic conductivity, mechanism (δ) has been discarded. In mechanism (γ) putting $m = 4$ the composition of the complex comes out to be $Ag(NH_3)_{4/3}$ which is considered as unplausible. In mechanism (α) while $m = 2$, x can have only unity as its value. So the complexes would have the formulæ $Ag_2NH_3PO_4^-$ and $AgNH_3^+$.

These appear to be plausible in view of the fact that the solid compounds of the type $AgCl\frac{1}{2}NH_3$ and $AgCl \cdot NH_3$ are known to exist.[3] In the remaining mechanism (β), since $m = 3$, the only plausible value for x is unity. So the formulæ for the complexes come to be $AgNH_3PO_4^=$ and $AgNH_3^+$. This also is plausible, so the mechanism (α) or (β) appears to be operating in the complex formation in the present case.

It is interesting to note that there is a sudden large increase in the solubility when the concentration of ammonia is increased to 0·5 M. The value of n increases to 1·68. This needs further investigation.

Summary

The equation used by Dey for the calculation of the formula of the complex compounds from solubility data is shown to be applicable in cases where either the complex formation is very weak or in cases where n is equal to unity. In the general case where the complex formation is considerable the graphical method gives more reliable values of n for the complex formation. The method has been applied to investigate the nature of the complexes formed in the silver phosphate-ammonia water system, the necessary solubility data having been obtained at 35°·5 C.

The author takes this opportunity to thank Dr. K. S. G. Doss, D.Sc., F.Inst.P., F.R.I.C., Physical Chemist, Indian Institute of Sugar Technology, Kanpur, for his kind suggestions and valuable help during the course of this work.

References

1. A. K. Dey .. *J. I. C. S.*, May 1947, 207.
2. Bury .. *J. S. C. I.*, 1922, **41**, 352 T.
3. Partington .. *Text-book of Inorganic, Chemistry*, p. 347.

NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXVI. Phytochemical Methods of Nuclear Oxidation

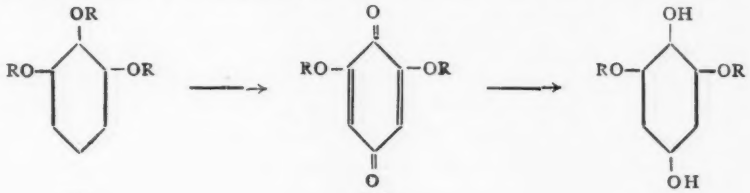
By T. R. Seshadri

(From the Department of Chemistry, Delhi University)

Received September 29, 1949

In Nature as well as in the laboratory oxidation is a fundamentally important process and is employed for a variety of purposes. The term nuclear oxidation has been used[1, 7] for the oxidation of a nuclear position of benzenoid systems resulting in the introduction of a fresh hydroxyl group. It is considered that the word ' hydroxylation ' is not suitable for this purpose because it has been used in a wider sense in the preparation of dye-intermediates and further it does not always signify the use of an oxidising agent. Nuclear oxidation seems to take place fairly freely in Nature and appears to be an essential phytochemical process in the evolution of anthoxanthins.[2] It may be relevant to mention here the view of Szent-Gyorgyi[3] that flavones form part of the oxidation-reduction chain in the plant cell.

A possible method that could be suggested for nuclear oxidation and that was also investigated earlier, involves the use of oxidising agents like chromic and nitric acids. Typical examples[4] are the conversion of pyrogallol-trimethyl and tribenzyl-ethers (I) to 2 : 6-dimethoxy and dibenzyloxyquinones (II) which could be subsequently reduced to the quinols (III). However, the application of this method is quite limited and it has been unsuccessful in the case of the anthoxanthins.[5] Further the reagents have no analogy with the phytochemical reagents available in the plants.



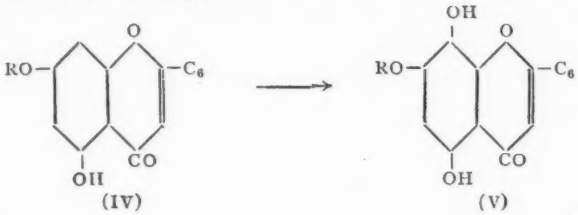
(I) (II) (III)

R = CH_3 or C_7H_7

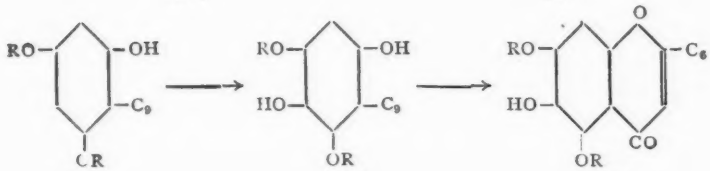
On the other hand, Elbs persulphate oxidation method has been found to be highly useful. The mechanism of this reaction has been recently discussed by Baker and Brown.[6] It introduces a fresh hydroxyl group in a reactive position of the flavone structure quite satisfactorily. The main results obtained are discussed in Part XIII[7] of this series under the headings

(1) Biogenesis of anthoxanthins, (2) Simplified methods of synthesis and (3) Study of chemical constitution. The important point in regard to this process is its directness for introducing a hydroxyl in a nuclear position and its appropriateness from the point of view of biogenesis. Persulphate is very closely analogous in its reaction to hydrogen peroxide[8] which could be accepted as a phytochemical reagent.

In the above mentioned discussion[7] the question of the variations in the condensed benzene ring of the flavone system was satisfactorily dealt with on the basis that nuclear oxidation involves both the fully closed pyrone compounds (IV) and the related open forms (VI) and that partial protection of the hydroxyl groups is effected earlier leaving a resistant hydroxyl group alone free to activate the concerned position. In these cases only para oxidation was necessary; this takes place readily in the laboratory with persulphate and in nature an analogous single stage process involving hydrogen peroxide could be suggested.

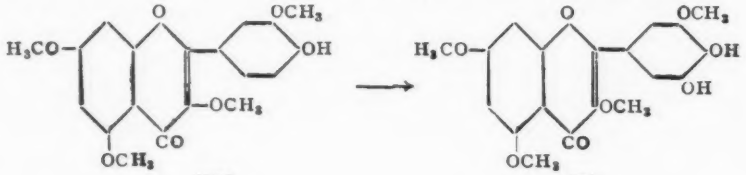


(IV) (V)



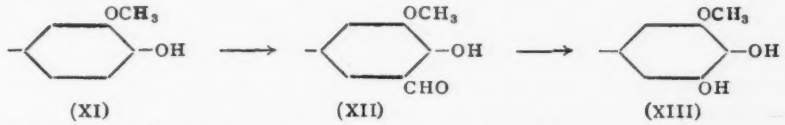
(VI) (VII) (VIII)

On the other hand, in regard to the side phenyl nucleus, as exemplified by the oxidation of quercetin into myricetin, ortho-oxidation is involved. The parallel case of cyanidin and delpihinidin in the anthocyanins has been discussed in detail by Robinson and his collaborators[9] using genetic evidence and the position is well established. But the oxidation of a quercetin derivative (IX) into (X) could not be achieved with persulphate.[10]



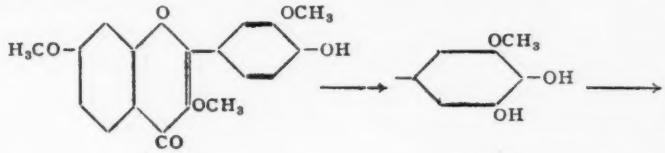
(IX) (X)

Even in simpler cases ortho-oxidation with this reagent was very unsatisfactory. Consequently an alternative procedure which would be more effective had to be considered. The following two stage process seemed to be suitable.

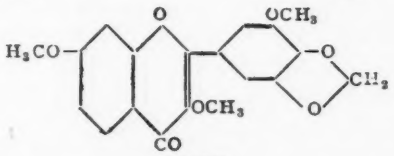


(XI) (XII) (XIII)

This has been confirmed not only by using the most favourable cases[11] of ortho oxidation, but also with the classical example[12] of quercetin oxidation to myricetin. Very satisfactory yields are obtained. For the first stage hexamine is used as the reagent and for the second stage (Dakin's reaction) hydrogen peroxide. The former may be considered to be a convenient form for bringing into reaction formaldehyde. Thus the reagents employed approximate phytochemical reagents closely. Incidentally the intermediate catechols can be conveniently methylenated to yield naturally occurring methylene ethers. As a typical naturally occurring example kanugin (XVI) has been synthesised from fisetin-tri-methyl ether (XIV).[13]

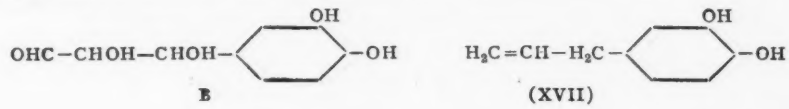


(XIV) (XV)



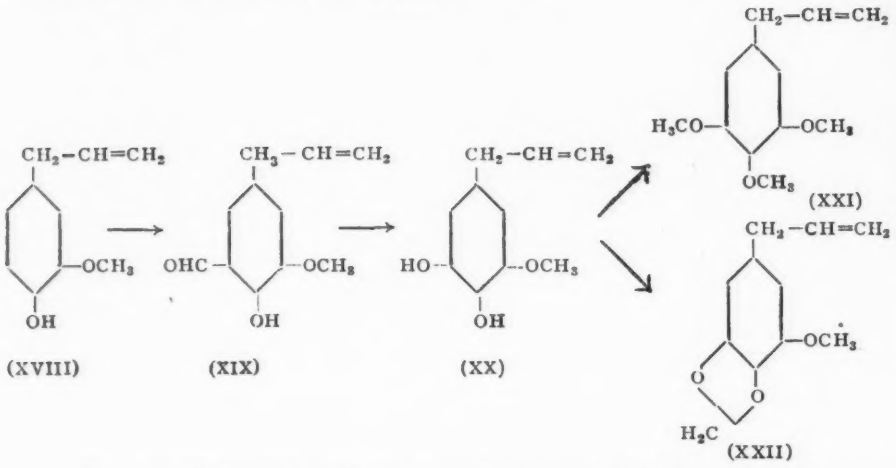
(XVI)

More recently this work has been extended to the components of essential oils which are classified as allyl (XVII) and propenyl benzene derivatives. Robinson[14] has drawn attention to the biogenetic similarity between the 9 carbon systems present in these and in the non-phloroglucinol part of anthocyanins and anthoxanthins. Both are considered to arise from the component B of the biogenetic precursor.

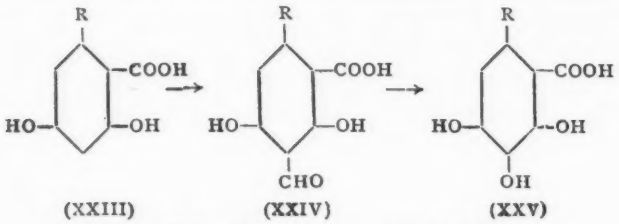


B (XVII)

The two stage ortho oxidation process is now found to proceed very satisfactorily with eugenol[15] (XVIII). This has led to a simplified synthesis of elemicin (XXI) and myristicin (XXII).

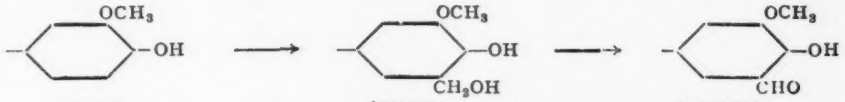


For considering this multi-stage mechanism as valid for phyto-chemical ortho-oxidation, support could be obtained from the study of lichen acids, a group of great chemical as well as physiological interest. In an earlier study of the biogenesis[16] of lichen depsides and depsidones it was suggested that formaldehyde was responsible for the introduction of CH_2OH, CHO and related groups in certain active nuclear positions yielding β-orcinol derivatives and the details were discussed. The important point relevant to the present purpose is that we could get here evidence for the existence of the aldehyde stage as a step in the introduction of a phenolic hydroxyl group. The fundamental units in these lichen acids are orsellinic acid or its homologues (XXIII). The aldehyde stage (XXIV) is found for instance in barbatolic acid and atranorin and corresponding hydroxy units (XXV) are present in sekikaic, homosekikaic, ramalinolic and boninic acids.



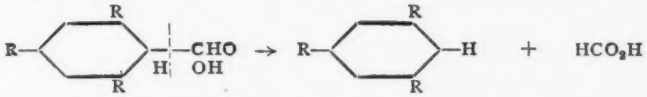
R=CH_3, C_3H_7, C_5H_{11}, C_7H_{15} or $CH_2—CO—C_5H_{11}$

In regard to the action of formaldehyde in these processes, the carbinol (XXVII) should represent the earliest stage. As well-known laboratory analogies could be mentioned the condensation of formalin with phenol, guaiacol, para and ortho cresols and *m*-hydroxy benzoic acid yielding the corresponding benzyl alcohols.[17] The next stage, *i.e.*, the conversion of the carbinol into the aldehyde (XXVIII) can also be brought about by formaldehyde. In the laboratory synthesis with hexamine such an oxidation is evidently involved. A process somewhat analogous to the Meerwein- Pondorff reaction can be suggested for the conversion of the alcohol (XXVII) into the aldehyde (XXVIII) by means of formaldehyde though the possibility of other oxidising agents available in the plant taking part in this oxidation also exists.

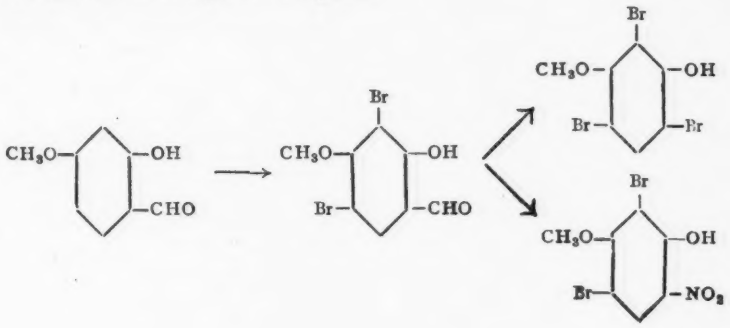


(XXVI) (XXVII) (XXVIII)

In the next stage the facility with which an aldehyde group is replaced by a phenolic hydroxyl group in Dakin's reaction has to be considered and explained. The same considerations will hold good where an acetyl group is involved instead of an aldehyde. In the first instance the presence of alkali may be expected to encourage the hydrolytic fission of aromatic aldehydes and ketones. The expulsion of a formyl group in warm acid or alkaline media has been considered to be common in polyhydroxy aldehydes.[18]

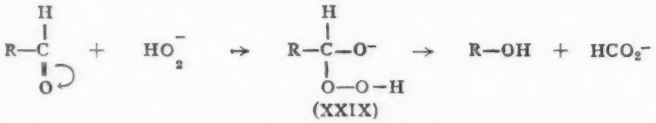


That a bromine atom or a nitro group could replace it more readily is shown by the following example;[19] bromine and nitric acid used in these reactions are well-known electrophilic reagents.



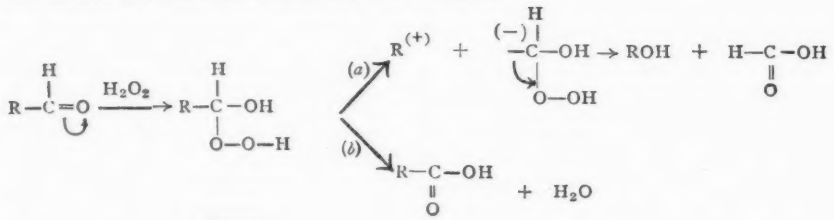
The smoothness of Dakin's reaction may be attributed to the combined effect of alkali and hydrogen peroxide, the former helping the removal of the aldehyde and the latter supplying the hydroxyl group for substitution. That this reagent is also electrophilic in its reaction with phenolic compounds has been recognised.[8]

The above simple explanation may not be quite adequate. Recently it has been considered that when reacting with aldehydes in the presence of bases hydrogen peroxide behaves as a nucleophilic reagent, HO_2^- being the active ion.[20] Based on this consideration the reaction can be represented as follows.



(XXIX)

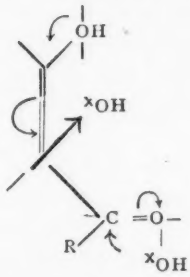
The experiments of Späth, *et al.*[21] would indicate that neither alkali nor a phenolic hydroxyl group is necessary. They have been able to carry out Dakin's reaction with non-hydroxylic aldehydes using an ether solution of hydrogen peroxide. The conditions are not favourable for the formation of the ion HO_2^-. But it has been suggested that structure (XXX) is probably formed as an intermediate. From their results it could be seen that actually benzaldehyde gives a very poor yield of phenol (0·7%) whereas aldehydes containing a number of methoxyls in certain suitable positions give much better yields (14-26%). But in no case is the yield so good as in the normal example using an ortho hydroxy aldehyde and alkaline hydrogen peroxide (about 80%). It would therefore appear that at some stage of the reaction nucleophilic activity of the polymethoxy phenyl system is involved though the beginning may be different. This stage may well be the fission of structure (XXIX) or (XXX).



(XXX)

Another significant result of the above experiments is the formation of the corresponding carboxylic acid as by-product, its yield being high when the yield of the phenol is low and *vice versa*. This is again explicable on the above mechanism. Where electron access to the concerned nuclear position is lacking or insufficient to encourage process (*a*), elimination of water (process *b*) takes place.

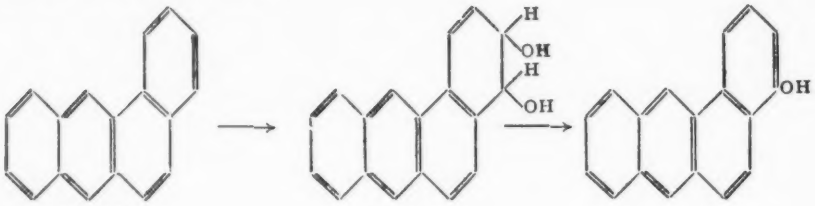
That both cationoid (electrophilic) and anionoid (nucleophilic) centres play their part in Dakin's reaction has earlier been indicated by Sir Robert Robinson in the course of his highly valuable address to the Chemical Society, London, on benzidine transformation and allied topics.[24] Considering hydrogen peroxide as the source of hydroxyl radicals, he has embodied this feature in his representation of the first phase of the reaction.



Summing up the discussion it could be stated that in phytochemical nuclear oxidation more than one process would appear to be employed. The single stage direct process is quite satisfactory for the para; though it may not be precluded for the ortho, it is very inefficient. On the other hand, the multistage process discussed above works very well for ortho oxidation. It may seem to be equally available for para oxidation also; but recent experiments using flavone derivatives[22] indicate that though *p*-hydroxy aldehydes could be obtained in good yields their further conversion into quinols takes place in low yields only.

It will be appropriate to mention here the interesting case of the biochemical nuclear oxidation of polycyclic (including carcinogenic) hydrocarbons in animal system, recently discussed by J. W. Cook and others.[23] This involves an altogether different mechanism. The initial products of metabolism are found to be diols resulting from the addition of two hydroxyl groups to an aromatic double bond (ethylenic activity). These are readily dehydrated to phenolic hydroxy derivatives of the original hydrocarbons. 1 : 2-Benzanthracene (XXXI) is used below as a typical example. The oxidation of these hydrocarbons in the laboratory using osmium tetroxide

resembles biochemical oxidation, but the position of the double bond attacked is found to be different.



(XXXI)

Summary

It is suggested that phytochemical nuclear oxidation involves several processes. (1) A single stage direct process which is satisfactory for the para oxidation of flavones and related compounds, the model being Elbs persulphate oxidation method, has already been discussed in detail in Part XIII. (2) A multistage process, an aldehyde being an intermediate stage which subsequently undergoes oxidation (Dakin's reaction), is illustrated by the recent synthesis of the flavonols, myricetin, robinetin and kanugin and essential oil components, elemicin and myristicin. Support for the existence of the stages can be obtained from a study of lichen acids. The mechanism of this process is discussed; it is quite suitable for ortho oxidations in flavones and related compounds, but the yields are rather poor in para-oxidations. Another multistage process involving ethylenic activity has been shown by Cook and others to be applicable to polycyclic hydrocarbons.

References

1. Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1947, **25**, 417.
2. ——— .. *Ibid.*, 1943, **18**, 222.
3. Szent-Gyorgyi .. *Studies on Biological Oxidations and Some of its Catalysts*, published by Barth, Leipsig, 1937, 67.
4. Grabe and Hess .. *Ann.*, 1905, **340**, 237.
   Baker, Nodzu and Robinson .. *J. C. S.*, 1929, 74.
5. Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1947, **25**, 418 and 419.
6. Baker and Brown .. *J. C. S.*, 1948, 2303.
7. Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1948, **28**, 1.
8. Discussion on Oxidation .. *Trans. Faraday Soc.*, 1946, **42**, 195 and 196.
9. Robinson, *et al.* .. *Phil. Trans. Roy. Soc.*, London, 1939, **230 B**, 149.
10. Rao, Seshadri and Thiruvengadam *Proc. Ind. Acad. Sci.*, A, 1948, **28**, 98.
11. ——— .. *Ibid.*, 1948, **28**, 100.
12. Row and Seshadri .. *Ibid.*, 1948, **28**, 210.
13. Row, Seshadri and Thiruvengadam *Ibid.*, 1949, **29**, 168.

14.	Robinson	..	*Nature*, 1936, **137**, 172.
15.	Rao, Seshadri and Thiruvengadam		*Proc. Ind. Acad. Sci.*, A, 1949, **30**, 114.
16.	Seshadri	..	*Ibid.*, 1944, **20**, 1.
17.	Manasse	..	*Ber.*, 1894, 2409.
	Hanus	..	*J. Pr. Chem.*, 1940 (ii), **155**, 317.
	Buehler, *et al.*	..	*J. A. C. S.*, 1944, 417; 1946, 574.
	Burawoy and Chamberlain	..	*J. C. S.*, 1949, 624.
18.	Robertson, *et al.*	..	*Ibid.*, 1949, 870.
19.	Rao, Srikantiah and Iyengar	..	*Ibid.*, 1929, 1578.
	Murti and Seshadri	..	*Proc. Ind. Acad. Sci.*, 1942, **16**, 135.
20.	Bunton, *et al.*	..	*Nature*, 1948, **161**, 172.
21.	Späth, *et al.*	..	*Ber.*, 1940, **73**, 935.
22.	Seshadri and Varadarajan	..	*Proc. Ind. Acad. Sci.*, under publication.
23.	Cook, *et al.*	..	*J. C. S.*, 1948, 170; *Chem. and Ind.*, 1948, 730.
24.	Robinson, R. (Sir)	..	*J. C. S.*, 1941, 220.

NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXVII. A New Synthesis of Norwogonin and Its Methyl Ethers

By T. R. Seshadri and S. Varadarajan

(*From the Department of Chemistry, Andhra University, Waltair*)

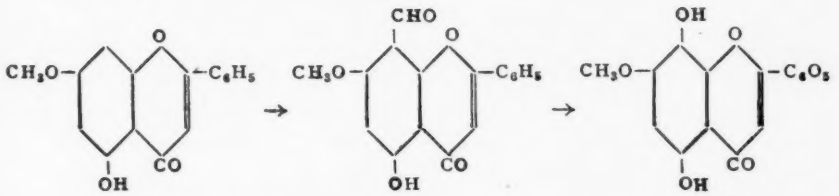
Received September 29, 1949

From the results obtained in previous parts[1-5] of this series, it has been established that the two stage oxidation process is definitely satisfactory for nuclear ortho-oxidation in flavones and related compounds. In these particular cases, no para position is free to undergo this oxidation. However, when in other cases a para position should be free, as already stated, a general consideration of the reactions involved would indicate that the method should be available for para oxidations also. No experiments have so far been done in the flavone series to test this point. Further, when an ortho as well as a para position are available, how this two stage process would function required careful investigation. It was also noticed that there was considerable difference[6] between 3-methoxy-7-hydroxy flavone and 7-hydroxy flavone in their reaction with hexamine and in their direct oxidation with alkaline persulphate. The yields in both the reactions were considerably higher with 3-methoxy-7-hydroxy flavone. The apparent influence of the methoxyl group in enhancing yields had to be examined, using other examples. Experiments carried out with reference to all these points are discussed in this paper.

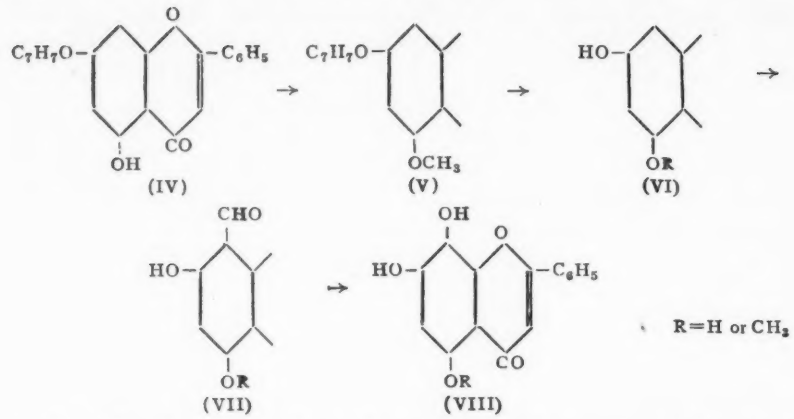
(*i*) *Oxidation of Tectochrysin*—To test the feasibility of the two stage oxidation process for para oxidation, tectochrysin (I) was chosen as a suitable example. It contains a hydroxyl in the 5-position which can activate both the 6-(ortho) and the 8-(para) positions. There are many simpler examples in which both the ortho and para positions are activated by a phenolic hydroxyl group. Phenol on treatment with formalin and alkali yields both saligenin and *p*-hydroxy benzyl alcohol.[7] Similarly salicylic acid when boiled with hexamine in acetic acid medium gives both the 3 and 5-aldehydo salicylic acids.[8]

It is now found that when tectochrysin (I) is condensed with hexamine in glacial acetic acid solution a single aldehyde (II) is obtained in 60% yield. The orientation of the aldehydo group has been determined as para

to the hydroxyl by treating the compound with alkaline hydrogen peroxide, when it is converted to isowogonin (III).[9] The identity of (III) has been confirmed by further methylation to 5:7:8-trimethoxy flavone. It is therefore established that the two stage process is available for para oxidations also in flavones and there is preferential activity of the 8-(para) position over the 6-(ortho). Incidentally a new synthesis of isowogonin is also effected. It should be noted, however, that in this instance of Dakin's reaction forming a quinol, the yield is rather low.



(*ii*) 5-*O-Methyl chrysin*.—It has been definitely established through experiments with flavones and chromones, that a 7-hydroxyl always activates the 8-position in the hexamine reaction.[6] Murti and Seshadri[4] found that even when the 8-position is occupied, a 7-hydroxyl does not activate the 6-position in this reaction. Experiments now carried out support these conclusions. 5-O-Methyl chrysin (VI, R=CH_3), isomeric with 7-hydroxy-3-methoxy flavone, is chosen in order to further investigate the activating influence of a methoxyl group. It is a new methyl ether of chrysin which was first obtained by Zemplen, *et al.*[10] by the methylation and hydrolysis of toringin, a 7-glucoside of chrysin. The attempts of the above authors to synthesise it starting from 2-methyl phloracetophenone were unsuccessful. The unreliability of this method has already been commented upon.[11] It has now been made by the methylation of 7-O-benzyl chrysin (IV)[12] to 7-O-benzyl-5-O-methyl chrysin (V) and subsequent debenzylation. The hexamine reaction proceeds satisfactorily with (VI, R=CH_3) giving the 8-aldehyde (VII, R=CH_3) in 65% yield which is comparable to the yield (70%) of the aldehyde from 7-hydroxy-3-methoxy flavone. It may be noted here that 7-hydroxy flavone provides only a 40% yield of the corresponding aldehyde.[6] The aldehyde (VII) is converted by Dakin's reaction into 7:8-dihydroxy-5-methoxy flavone (VIII, R = CH_3), a second isomer of wogonin, now named allowogonin. The constitution of (VIII) is proved by methylation to 5:7:8-trimethoxy flavone.[9] These experiments, therefore, confirm the favourable influence of a methoxyl group in the hexamine reactions.



(*iii*) *Chrysin.*—It has been shown in the above paragraphs that the hydroxyl in the 5-position, and that in the 7-position both activate the 8-position. The combined influence of both the 5- and 7- hydroxyls has been shown to be favourable in the case of persulphate oxidations.[13, 9] This point has now been tested using the aldehyde method. Chrysin (VI, R = H) is an appropriate example for this purpose. It yields, as expected, the aldehyde (VII, R=H) in 90% yields. It is converted into norwogonin (VIII, R=H) by alkaline hydrogen peroxide; the yields in this reaction are again low probably due to the presence of a quinol structure in the final product. However this constitutes another synthesis of norwogonin.

Experimental

Chrysin and tectochrysin required for these experiments were prepared by the procedure recently described by Rao, Rao and Seshadri.[9]

Tectochrysin aldehyde (*II*).—Tectochrysin (1 g.) was dissolved in glacial acetic acid (20 c.c.) and heated on a boiling water-bath with hexamine (3 g.) for six hours. The solution which was pale red at the beginning turned slowly brown. To the hot solution was added boiling hydrochloric acid (1 : 1, 30 c.c.) and the mixture allowed to cool. On dilution with water (200 c.c.) a sticky solid separated out. More of it was formed when the solution was neutralised with sodium hydroxide. It slowly changed to a bright yellow powder on stirring well. It was filtered and washed with water. On crystallisation from a mixture of alcohol and ethyl acetate, it separated in the form of short yellow needles which did not melt below 340°. Yield 0·6 g. (Found: C, 68·6, H, 4·4; $C_{17}H_{12}O_5$ requires C, 68·9, H, 4·1%). It was soluble in alcohol and acetic acid and sparingly soluble in ethyl acetate,

benzene and acetone. It gave an orange red colour with alcoholic ferric chloride. The dinitrophenylhydrazone of the aldehyde crystallised from alcohol as dark red prisms and melted at 160-61° (decomp.).

Isowogonin (*III*).—The above aldehyde (1 g.) was dissolved in a mixture of pyridine (40 c.c.) and sodium hydroxide (3·7 c.c. of 1 N) and 6% hydrogen peroxide (5 c.c.) added slowly to the solution kept at 40° and with a stream of nitrogen passing through the flask to displace air. After allowing to stand at this temperature for 30 minutes, the solution was cooled and acidified. The pale brown solid product was filtered, washed with water and crystallised from ethyl acetate, when it came out as bright yellow needles melting at 234-35°, alone or in admixture with an authentic sample of isowogonin.[9] Yield 0·2 g. In its colour reactions and other properties it was identical with isowogonin.

On methylation with dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium, it yielded 5: 7: 8-trimethoxy flavone, m.p. 167-68°.[9]

7-O-*Benzyl*-5-O-*methyl chrysin* (*V*).—7-O-Benzyl chrysin (1·5 g.) was dissolved in dry acetone (200 c.c.) and refluxed with dimethyl sulphate (0·7 c.c.) and potassium carbonate (10 g.) for 18 hours. Acetone was distilled off and water added to the residue and filtered. The undissolved pale brown solid, on crystallisation from benzene-petroleum ether mixture came out as colourless rectangular rods melting at 184-85°. It did not give any colour with alcoholic ferric chloride. Yield 1·3 g. (Found: C, 76·7, H, 5·1; $C_{23}H_{18}O_4$ requires C, 77·1, H, 5·0%).

5-O-*Methyl chrysin* (*VI*, $R=CH_3$).—The above compound (V) (1 g.) was dissolved in glacial acetic acid (20 c.c.) and concentrated hydrochloric acid (14 c.c.) added and the mixture kept in a boiling water-bath for one hour. It was then diluted with water (100 c.c.) and the solid that separated out was filtered. Yield 0·5 g. On crystallisation from alcohol, it came out as thin colourless rhombic plates melting at 278-79°. It did not give any colour with alcoholic ferric chloride and dissolved in alkali to give a pale yellow solution. (Found: C, 71·2, H, 4·5; $C_{16}H_{12}O_4$ requires C, 71·6, H, 4·5%.)

5-O-*Methylchrysin*-8-*aldehyde* (*VII*, $R=CH_3$).—5-O-Methyl chrysin (VI) (2 g.) was heated on a boiling water-bath with glacial acetic acid (40 c.c.) and hexamine (6 g.) for 6 hours. Boiling hydrochloric acid (1 : 1, 40 c.c.) was added to the hot brown solution. On cooling a pale yellow crystalline solid separated out. The solution was diluted with water and the precipitated solid filtered off. Yield 1·3 g. It crystallised from alcohol containing

a few drops of acetic acid as small pale yellow needles, m.p. 295° (decomp.). It gave a red colour with alcoholic ferric chloride. (Found: C, 68·7, H, 4·4; $C_{17}H_{12}O_5$ requires C, 68·9, H, 4·1%.)

The dinitro-phenylhydrazone of the aldehyde, prepared by heating an alcoholic solution of the susbstance with dinitrophenylhydrazine, melted at 172–73° (decomp.).

7: 8-*Dihydroxy*-5-*methoxy flavone* (*Allowogonin*) (*VIII*, $R=CH_3$).—The above aldehyde (0·5 g.) was dissolved in pyridine (25 c.c.) and aqueous sodium hydroxide (2 c.c. of 1 N). To the cooled solution was added hydrogen peroxide (3 c.c. of 6%) drop by drop, with shaking. It was left at room temperature for 2 hours and then acidified with ice-cold hydrochloric acid. The greenish yellow solid product was filtered and washed with water. Ether extraction of the filtrate gave some more of the substance. Yield 0·3 g. On crystallisation from rectified spirits, 7: 8-dihydroxy-5-methoxy flavone separated as pale yellow, long fine needles melting at 132°. It gave a greenish brown colour with alcoholic ferric chloride and a reddish brown solution in aqueous sodium hydroxide. (Found: C, 67·3, H, 4·6; $C_{16}H_{12}O_5$ requires C, 67·6, H, 4·2%.)

On methylation with excess of dimethyl sulphate and potassium carbonate in dry acetone medium, it yielded 5: 7: 8-trimethoxy flavone melting at 167-68°. The mixed melting point with an authentic sample of the trimethyl ether was not depressed.

5: 7-*Dihydroxy-flavone*-8-*aldehyde* (*VII*, $R=H$).—Chrysin (1 g.) was dissolved in glacial acetic acid (20 c.c.) and heated with hexamine (3 g.) on a boiling water-bath. The solution which was originally red, turned deep reddish brown and after two hours began to deposit a yellow solid. The heating was continued for another four hours and the hot solution mixed with boiling hydrochloric acid (30 c.c.) (1 : 1). It was then cooled and diluted with water (100 c.c.) and the bright yellow solid filtered. Yield 0·9 g. When crystallised from acetic acid, it came out as yellow rectangular plates which did not melt below 350°. It gave an orange colour with alcoholic ferric chloride, was insoluble in alcohol and benzene and very sparingly soluble in ethyl acetate and acetone. (Found: C, 67·9, H, 3·9; $C_{16}H_{10}O_5$ requires C, 68·1, H, 3·5%.)

The dinitro phenylhydrazone prepared by refluxing an acetic acid solution of the aldehyde with alcoholic dinitrophenyl-hydrazine for 2 hours, melted at 314° (decomp.).

5: 7: 8-*Trihydroxy flavone* (*Norwogonin*) (*VIII*, $R=H$).—The above aldehyde (1 g.) was dissolved in pyridine (30 c.c.) and aqueous sodium hydroxide

(3·7 c.c. of 1 N) and the solution was cooled to 10°. Hydrogen peroxide (6 c.c. of 6%) was added drop by drop when the red colour of the solution changed to deep brown. After 20 minutes, it was acidified and the brown solid filtered. When twice crystallised from ethyl acetate-petroleum ether mixture, it separated as golden yellow rectangular plates and prisms melting at 258-59°, alone or when mixed with an authentic sample of norwogonin. Yield 0·15 g.

Summary

(1) Chrysin, (2) tectochrysin and (3) 5-O-methyl chrysin are subjected to the two stage oxidation process. All of them give good yields of the corresponding 8-aldehydes. In (2) the 8-position (para) is predominantly more reactive than the 6-position (ortho). In (1) and (3) the favourable influence of a hydroxyl and a methoxyl in the 5-position is exerted. The Dakin's reaction gives poor yields if the product is a quinol and good yields if it is a catechol. Experiments with (1) and (2) lead to the conclusion that the two stage method is available for para oxidations though the yields are poor.

References

1. Row, Seshadri and Thiruvengadam .. *Proc. Ind. Acad. Sci.*, A, 1948, **28**, 98.
2. Rao and Seshadri .. *Ibid.*, 1948, **28**, 210.
3. Row, Seshadri and Thiruvengadam .. *Ibid.*, 1949, **29**, 168.
4. Murti and Seshadri .. *Ibid.*, 1949, **29**, 221.
5. ———— .. *Ibid.*, 1949, **30**, 12.
6. Rangaswami and Seshadri .. *Ibid.*, 1939, **9**, 7.
   Narasimhachari, Row and Seshadri .. *Ibid.*, 1948, **27**, 37.
7. Mannasse .. *Ber.*, 1894, **27**, 2411.
8. Duff and Bills .. *J. C. S.*, 1934, 1305.
9. Rao, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1947, **25**, 427.
10. Zemplen, Bognar and Mechner .. *Ber.*, 1944, **77** B, 99.
11. Rajagopalan, *et al.* .. *Proc. Ind. Acad. Sci.*, A, 1949, **29**, 9.
12. Rao, Rao and Seshadri .. *Ibid.*, 1947, **26**, 13.
13. Rao and Seshadri .. *Ibid.*, 1947, **25**, 421.

335-49 Printed at The Bangalore Press, Mysore Road, Bangalore City, by G. Srinivasa Rao, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.

INDEX TO VOL. XXX (A)

AUTHORS' INDEX

Anantakrishnan, S. V. .. Characteristic frequency and chemical reactivity, 23.

Balakrishna, K. J., Seshadri, T. R., and Viswanath, G. Nuclear oxidation in flavones and related compounds, XXV, 120.

.. Formation of quinones by oxidative demethylation, IV, 163.

Bhatnagar, Shanti Swarup *See* Saksena and Bhatnagar.

Chariar, V. R. .. On the skewness of distribution of the generators of a ruled surface, 49.

Chiplonkar, M. W., and Hattiangadi, M. S. On the reflection of atmospherics from the ionosphere at night, II, 223.

Gakhar, K. L. .. *See* Rao and Gakhar.

Gokhale, G. S., Rao, A. S., and Thatte, R. P. Measurement of high altitude vertical cosmic ray intensity, at New Delhi, India, 19° North, geomagnetic latitude, 184.

Hattiangadi, M. S. .. *See* Chiplonkar and Hattiangadi.

Hattiangadi, G. S. .. Solubility of some sodium soaps in pinene, 320.

Kapur, N. S. .. *See* Singh and Kapur.

Katti, P. K. .. Studies in colloid optics, II, 35.

Manhas, K. M. S. .. *See* Singh and Manhas.

.. *See* Singh and others.

Murti, V. V. Sreerama, and Seshadri, T. R. Nuclear oxidation in flavones and related compounds, XXI, 12; XXII, 78; XXIII, 107.

Muthuswami, T. N. .. Sapphirine (*Madura*), 295.

Narain, Hari .. *See* Saksena and Narain.

Narasimhachari, N., and Seshadri, T. R. A new synthesis of flavones, 151.

.. Synthetic experiments in the benzopyrone series, XI, 216.

.. A note on the components of the bark of *Prunus puddum*, 271.

Narlikar, V. V., and Prasad, Ayodhya The Doppler effect in the field of a thick spherical shell, 181.

Nayar, M. R., and Pande, C. S.	Formation of complex compounds between lead nitrate and alkali nitrates, VII, 255; VIII, 259.
Nayar, M. R., Pande, C. S., and Srivastava, S. S.	Formation of complex compounds between lead nitrate and alkali nitrates, VI, 251.
Pande, C. S. ..	*See* Nayar and others.
..	*See* Nayar and Pande.
Prasad, Ayodhya ..	*See* Narlikar and Prasad.
Press, D. C. ..	Thermal expansion of fluorspar and iron pyrite, 284.
Puri, (Miss) Vimla ..	*See* Singh and others.
Rajagopalan, S., Seshadri, T. R., and Varadarajan, S.	A new synthesis of asaronic acid and aldehyde and their derivatives, 265.
Raman, C. V., and Ramaseshan, S.	The Christiansen experiment with spherical particles, 211.
..	Diffraction of light by transparent spheres and spheroids: the Fresnel patterns, 277.
Ramaseshan, S. ..	*See* Raman and Ramaseshan.
Rao, A. S. ..	*See* Gokhale and others.
Rao, D. A. A. S. Narayana	Dielectric constants of crystals, III, 82.
..	Ionic polarisation in crystals: additivity in double salts, 317.
Rao, K. Visweswara, and Seshadri, T. R.	Colour reaction of certain phenolic ethers and their derivatives with nitric acid, 30.
Rao, K. Visweswara, Seshadri, T. R., and Thiruvengadam, T. R.	Nuclear oxidation in flavones and related compounds, XXIV, 114.
Rao, P. S., and Gakhar, K. L.	A note on the preparation of quinacetophenone, 327.
Rao, R. V. G. Sundara ..	The elastic constants of sodium tartrate and Rochelle salt, 173.
..	Elastic constants of sodium thiosulphate, 302
Saksena, B. D., and Bhatnagar, Shanti Swarup	Comparison of the infra-red activities of the four Raman-inactive vibrations in α-quartz, 308.
Saksena, B. D., and Narain, Hari	Raman and infra-red spectra of β-quartz, 128.
Saraswat, H. C. ..	Formula of complex compounds from solubility data, 329.

Seshadri, T. R.	..	*See* Balakrishna and others.
	..	*See* Murti and Seshadri.
	..	*See* Narasimhachari and Seshadri.
	..	Nuclear oxidation in flavones and related compounds, XXVI, 333.
	..	*See* Rajagopalan and others.
	..	*See* Rao and others.
	..	*See* Rao and Seshadri.
Seshadri, T. R., and Subramanian, S. Sankara		Chemical investigation of Indian lichens, VIII, 15; IX, 62; X, 67.
Seshadri, T. R., and Varadarajan, S.		Nuclear oxidation in flavones and related compounds, XXVII, 342.
Shah, K. H., Tilak, B. D., and Venkataraman, K.		Sulphur dyes and sulphurised vat dyes, II, 1.
Shah, R. C.	..	*See* Virkar and Shah.
Singh, B. K., and Kapur, N. S.		Studies on the dependence of optical activity on chemical constitution, XXXIV, 237.
Singh, B. K., and Manhas, K. M. S.		Studies on the dependence of optical activity on chemical constitution, XXIII, 87.
	..	The refractive dispersive power of organic compounds, II, 140.
Singh, B. K., Manhas, K. M. S., Singh, Mahan, and Puri, (Miss) Vimla		The diamagnetic susceptibilities of phthalic acid and phthalic anhydride, 103.
Singh, Mahan	..	*See* Singh and others.
Srivastava, S. S.	..	*See* Nayar and others.
Subramanian, S. Sankara		*See* Seshadri and Subramanian.
Thatte, R. P.	..	*See* Gokhale and others.
Thiruvengadam, T. R.	..	*See* Rao and others.
Tilak, B. D.	..	*See* Shah and others.
Varadarajan, S.	..	*See* Rajagopalan and others.
	..	*See* Seshadri and Varadarajan.
Venkataraman, K.	..	*See* Shah and others.
Venkayya, E.	..	A new occurrence of Mahadevite, 74.
Virkar, V. V., and Shah, R. C.		Chromones, II, 57.
Viswanath, G.	..	*See* Balakrishna and others.
Vrkljan, V. S.		Über das magnetische moment des mesons, 205.

TITLE INDEX

Asaronic acid and aldehyde and their derivatives, a new synthesis (Rajagopalan and others), 265.

Atmospherics, reflection, from the ionosphere at night, II (Chiplonkar and Hattiangadi), 223.

Benzopyrone series, synthetic experiments, XI (Narasimhachari and Seshadri), 216.

Christiansen experiment with spherical particles (Raman and Ramaseshan), 211.

Chromones, II (Virkar and Shah), 57.

Colloid optics, studies, II (Katti), 35.

Complex compounds, formation, between lead nitrate and alkali nitrates, VI (Nayar and others), 251; VII, VIII (Nayar and Pande), 255, 259.

Complex compounds, formula, from solubility data (Saraswat), 329.

Cosmic ray intensity, high altitude vertical, at New Delhi, India, 19° North, geomagnetic latitude, measurement (Gokhale and others), 184.

Dielectric constants of crystals, III (Rao), 82.

Diffraction of light by transparent spheres and spheroids: the Fresnel patterns (Raman and Ramaseshan), 277.

Doppler effect in the field of a thick spherical shell (Narlikar and Prasad), 181.

Elastic constants of sodium tartrate and Rochelle salt (Rao), 173.

Elastic constants of sodium thiosulphate (Rao), 302.

Ethers, phenolic, certain, and their derivatives, colour reaction, with nitric acid (Rao and Seshadri), 30.

Flavones, a new synthesis (Narasimhachari and Seshadri), 151.

Frequency, characteristic, and chemical reactivity (Anantakrishnan), 23.

Ionic polarisation in crystals: additivity in double salts (Rao), 317.

Lichens, Indian, chemical investigation, VIII, IX, X (Seshadri and Subramanian), 15, 62, 67.

Mahadevite, a new occurrence (Venkayya), 74.

Mesons, über das magnetische moment (Vrkljan), 205.

Nuclear oxidation in flavones and related compounds, XXI, XXII, XXIII (Murti and Seshadri), 12, 78, 107; XXIV (Rao and others), 114; XXV (Balakrishna and others), 120; XXVI (Seshadri), 333; XXVII (Seshadri and Varadarajan), 342.

Optical activity, dependence, on chemical constitution, studies, XXXIII (Singh and Manhas), 87; XXIV (Singh and Kapur), 237.

Organic compounds, the refractive dispersive power, II (Singh and Manhas), 140.

Phthalic acid and phthalic anhydride, the diamagnetic susceptibilities (Singh and others), 103.

Prunus puddum, bark, components, a note (Narasimhachari and Seshadri), 271.

Quinacetophenone, preparation, a note (Rao and Gakhar), 327.

Quinones, formation, by oxidative demethylation, IV (Balakrishna and others), 163.

Raman and infra-red spectra of β-quartz (Saksena and Narain), 128.

Raman-inactive vibrations in α-quartz, four, comparison of the infra-red activities (Saksena and Bhatnagar), 308.

Sapphirine (*Madura*) (Muthuswami), 295.

Sodium soaps, some, solubility, in pinene (Hattiangdi), 320.

Sulphur dyes and sulphurised vat dyes, II (Shah and others), 1.

Surface, ruled, generators, on the skewness of distribution (Chariar), 49.

Thermal expansion of fluorspar and iron pyrite (Press), 284.

NOTICE TO AUTHORS

Scientific papers intended for publication in the *Proceedings of the Indian Academy of Sciences* can be accepted only when they are communicated by a Fellow of the Academy whose duty shall be to satisfy himself that such communications are fit to be read at the Meeting of the Academy and published in its *Proceedings*.

Papers should not ordinarily exceed fifty pages of foolscap. MSS. should be either typewritten or written in legible hand on one side of the paper. All papers should be carefully revised by the authors and should be absolutely in final form for printing. Position for text-figures should be indicated. Each paper shall conclude with a critical summary not exceeding 350 words.

Drawings, diagrams or other illustrations should be made on larger scale (preferably) twice the size than the ones in which they are intended to appear. They should be done in Indian ink on bristol board with lettering in pencil. Scale of magnification of camera lucida tracings should be indicated by the side of drawings. In certain special cases arrangements will also be made for monochrome lithographic and other colour plates. Reduction of illustrations desired should be indicated in pencil. Appropriate legends should accompany all drawings. Names of authors are to be marked in pencil on the left-hand corner of drawing sheets. Photomicrographs should be securely mounted with colourless paste.

All tables, quotations and footnotes which will be set hereafter (beginning from Vol. I, No. 2) in types smaller than the text, should be typewritten on separate sheets and placed with the text in proper sequence. Footnotes should be numbered in Arabic numerals.

References to literature in the text should be given, whenever possible, in chronological order, only the names of authors and years of publication, in brackets, being given. They should be cited in full after the summary, the authors' names following in alphabetical order. Thus,

Name or Names of author; Name of Journal (abbreviation) with a single underline; Year of publication; Number of Volume with a double underline, and lastly page. The following would be a useful illustration:—

Bergmann and Stather . . . . . Z. Physiol. Chem., 1926, 152, 189.

Two copies of slip-proof and wherever possible, a page proof for final revision will be sent to authors. All corrections are best made on the slip-proof which should be transmitted to the Office of the Academy. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.

Authors will be supplied with reprints of their papers at cost price, if intimation is given at the time of returning the slip-proof.

All the blocks printed in the *Proceedings* will be offered to the respective authors at a price of 25% of the actual cost of preparing the blocks *plus* the packing and postal charges or railway freight to be incurred for despatching them, it being understood that authors should give due acknowledgment to the Academy whenever such blocks are reproduced in other journals.

The original drawings and plates of blocks appearing in the *Proceedings* will be returned to such of the authors as may require them provided the cost of despatching such originals is borne by them.

CONTENTS

PAGE

Diffraction of Light by Transparent Spheres and Spheroids: The Fresnel Patterns . . . . . Sir C. V. Raman and S. Ramaseshan 277

Thermal Expansion of Fluorspar and Iron Pyrite . . . . D. C. Press 284

Sapphirine—(*Madura*) . . . . . T. N. Muthuswami 295

Elastic Constants of Sodium Thiosulphate . . . . R. V. G. Sundara Rao 302

Comparison of the Infra-Red Activities of the Four Raman-Inactive Vibrations in *a*-Quartz. Bishambhar Dayal Saksena and Shanti Swarup Bhatnagar 308

Ionic Polarisation in Crystals: Additivity in Double Salts . . . . . D. A. A. S. Narayana Rao 317

Solubility of Some Sodium Soaps in Pinene . . . . Gopal S. Hattiangdi 320

A Note on the Preparation of Quinacetophenone . . . . . P. S. Rao and K. L. Gakhar 327

Formula of Complex Compounds from Solubility Data . . H. C. Saraswat 329

Nuclear Oxidation in Flavones and Related Compounds. Part XXVI. Phytochemical Methods of Nuclear Oxidation . . . . . T. R. Seshadri 333

Nuclear Oxidation in Flavones and Related Compounds. Part XXVII. A New Synttesis of Norwogonin and Its Methyl Ethers . . . . . T. R. Seshadri and S. Varadarajan 342